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COMMITTEE ON PAPERS AND PUBLICATIONS.

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A New Electrolytic Stand. By George L. Hough.

A Collector for Distillation of Ammonia from Water. By F. P. Dunnington.

Boric Acid Determination. By Thomas S. Gladding.

A Moist Combustion Method of Determining Carbon in Steel. By Geo. Auchy.

Comparison of the Standard Methods for the Estimation of Starch. By H. W. Wiley and W. H. Krug.

The Solubility of the Pentosans in Reagents Employed in Estimating Starch. By W. H. Krug and H. W. Wiley.

On the Photometric Power of Petroleum Burning Oils. By C. F. Mabery and E. C. Jewett.

Preliminary Report of the Committee on Coal Analysis. By W. F. Hillebrand, C. B. Dudley, and W. A. Noyes.

Some Properties of Zirconium. By F. P. Venable and A. W. Belden.

Ammonium Selenide. By Victor Lenher and Edgar F. Smith.

Electrolytic Determinations. By Edgar F. Smith and Daniel L. Wallace.

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THE JOURNAL

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AMERICAN CHEMICAL SOCIETY.

FIFTH ANNUAL REPORT OF THE COMMITTEE ON ATOMIC WEIGHTS. RESULTS PUBLISHED DURING 1897.

BY F. W. CLARKE.

Received January 20, 1898.

To the Members of the American Chemical Society:

During 1897 comparatively few new determinations of atomic weights have appeared. The data given are as follows:

Carbon.—Scott[1] has carefully studied the determinations of the atomic weight of carbon which depend upon the combustion of the element and the weight of the dioxide formed, and has discovered an important correction. This is due to the considerable change of volume in the potash solution produced by the absorption of carbon dioxide, which involves a notable change in the reduction of the weighings to a vacuum. Scott has measured the amount of this change, and has applied it to the work of his predecessors with the subjoined results. In each case the values given are the means of the several experiments recorded.

	Uncorrected.	Corrected.
Dumas and Stas	11.9975	11.9938
Erdmann and Marchand	12.0093	12.0054
Roscoe	12.0029	11.9973
Friedel	12.0112	12.0056
Van der Plaats	12.0031	12.0018
Mean,	12.0048	12.0008

[1] *J. Chem. Soc.*, 71, 550, May, *1897.*

These values are based upon O = 16; with O = 15.879, the corrected mean result becomes C = 11.910.

Scott further criticises in detail the determinations by Stas which depend upon the combustion of carbon monoxide, and shows that they require possible corrections and involve various uncertainties. He concludes "that the atomic weight of carbon is by no means one of those most accurately known, and that a careful revision of it is imperative."

Nitrogen, Chlorine, and Silver.—Leduc[1], on the basis of his density determinations, assumes N = 14.005 when O = 16. Applying this to the determinations by Stas of the ratios Ag : Cl, $AgCl : O_2$, and $AgCl : NH_4Cl$, he finds a discrepancy of about one part in 320. That is, the work of Stas gives N = 14.044 instead of 14.005. This disagreement Leduc attributes to the presence of occluded oxygen, as pointed out by Dumas, in the silver used by Stas. For this he assumes a correction, and then, combining his value for nitrogen with the data given by Stas, he computes H = 1.0076, Cl = 35.470, and Ag = 107.916. The correction applied by Leduc seems to be somewhat uncertain; and it is doubtful whether his determination of the density of nitrogen is entitled to greater weight than the other data which are involved in the calculations.

Aluminum.—In the third and fourth reports of this committee Thomsen's data for the atomic weight of oxygen are given. In these determinations oxygen and hydrogen were compared with aluminum as an intermediary; but the aluminum used was not absolutely pure. Had it been pure, the atomic weight of the metal, with reference to the two gases, could have been computed.

Thomsen now[2] gives the data necessary for the comparison, and deduces the atomic weight of aluminum. The impurities are determined, and corrections for them applied. There is also a correction for the change in volume of the potash solution in which the metal was dissolved. Applying the corrections, Thomsen finds that 0.99897 gram pure aluminum correspond to 0.11195 gram of hydrogen. Hence, with H = 1,

$$Al = 26.770.$$

1 *Compt. rend.*, 125, 299, August 2, *1897*.
2 *Ztschr. anorg. Chem.*, 15, 447.

Again, 0.99897 gram of metal is equivalent to 0.88824 gram of oxygen. Hence, with O = 16,

$$Al = 26.992.$$

These two values, referring to the two standard units, are determined independently of each other, and are independent of any measured ratio between O and H. They are notably lower than the values computed by myself from Mallet's data, 26.91 and 27.11, and possibly should supplant the latter. This question, however, needs further discussion, and probably some additional experiments.

Nickel.—Atomic weight determined by Richards and Cushman,[1] from analyses of the anhydrous, sublimed bromide, $NiBr_2$. This substance is shown by the authors to be perfectly suited to the purpose of the investigation. The method of analysis was in all essential respects that used by Richards in other researches of the same kind, and was partly gravimetric and partly volumetric. On the one hand, the ratio $2AgBr : NiBr_2$ was determined; on the other, the ratio $2Ag : NiBr_2$. All weighings were reduced to a vacuum. The results, in three series, were as follows:

FIRST SERIES.

Weight $NiBr_2$.	Weight AgBr.	Atomic weight Ni.
2.26113	3.88769	58.646
2.80668	4.82431	58.708
1.41317	2.42880	58.716
1.71759	2.95307	58.650
2.48565	4.27357	58.651
4.32997	7.44280	58.700
2.18072	3.74856	58.693
	Mean,	58.680

SECOND SERIES.

Weight $NiBr_2$.	Weight AgBr.	Atomic weight Ni.
3.28039	5.63892	58.691
2.70044	4.64208	58.686
3.38230	5.81391	58.698
1.33459	2.29435	58.670
1.25054	2.14963	58.693
1.32778	2.27384	58.690
2.24452	3.85805	58.705
	Mean,	58.690

[1] *Proc. Amer. Acad.*, **33**, 97, November, *1897*.

THIRD SERIES.

Weight $NiBr_2$.	Weight Ag.	Atomic weight Ni.
3.28039	3.23910	58.701
2.70044	2.66636	58.709
3.38230	2.33990	58.689
1.33459	1.31787	58.689
1.25054	1.23482	58.698
1.32278	1.30629	58.675
2.24452	2.21652	58.676
	Mean,	58.691

From all these data the authors conclude that the atomic weight of nickel cannot be far from 58.69 when O = 16, or 58.25 if O = 15.88.

From series two and three 15.32086 grams of silver give 26.67078 grams of bromide. Hence the percentage of silver in silver bromide is 57.444, which agrees with the value 57.445 found by Stas. This is a good check upon the accuracy of the work.

Cobalt.—The atomic weight determinations by Richards and Baxter[1] are in all essential respects like those of nickel which have just been cited. The three series of data are as follows:

FIRST SERIES.

Weight $CoBr_2$.	Weight AgBr.	Atomic weight Co.
2.25295	3.86818	58.950
2.88763	4.95732	58.975
1.88806	3.24056	59.026
	Mean,	58.984

SECOND SERIES.

Weight $CoBr_2$.	Weight AgBr.	Atomic weight Co.
1.33564	2.29296	58.975
2.58129	4.43095	58.998
2.84382	4.88135	59.009
1.83722	3.15368	59.000
2.68584	4.61046	58.996
3.18990	5.47607	58.982
2.88914	4.95943	58.997
2.32840	3.99706	58.987
1.91703	3.29053	59.010
	Mean,	58.995

[1] *Proc. Amer. Acad.*, 33, 115, December, *1897*.

THIRD SERIES.

Weight $CoBr_2$.	Weight Ag.	Atomic weight Co.
1.33564	1.31702	59.002
2.58129	2.54585	58.955
2.84382	2.80449	58.977
1.83722	1.81170	58.991
2.68584	2.64879	58.969
2.88914	2.84891	58.998
2.32840	2.29593	59.003
1.91703	1.89033	58.999
	Mean,	58.987

If O = 16, Co = 58.99, as the outcome of all the series. If O = 15.88, Co = 58.55. From the data in series two and three the percentage of silver in silver bromide is 57.446, while Stas gives 57.445. The last five experiments, which are the best, give 57.447. This check on the accuracy of the work is therefore satisfactory.

Tungsten.—The investigation by Hardin[1] is rather the scrutiny of a method than an attempt to accurately fix an atomic weight. Most of the determinations of the atomic weight of tungsten have been based upon analyses or syntheses of the trioxide; and this substance is now shown to be exceedingly untrustworthy as regards the measurement of this constant. Hardin has made sixty-four determinations with the trioxide, in seventeen groups or series, using material from various sources, and working under a great variety of conditions. The values found range from W = 183.51 to W = 185.00, when O = 16, the average of all being 184.106. The same discordance appears upon comparing the results obtained by previous investigators, and it seems to be partly due to absorptions of tungsten or its oxide by the boat in which the reductions or oxidations were effected, and partly to the presence of nitrogen in the trioxide when the latter was prepared from ammonium tungstate. At all events, the method is unsuited to its purpose, and the atomic weight of tungsten needs thorough reinvestigation by means of other processes.

Cerium.—The atomic weight of this metal has been redetermined by Wyrouboff and Verneuil,[2] upon material purified by

[1] This Journal, 19, 657, August, *1897*.

[2] *Bull. Soc. Chim.* [3], 17, 679.

an elaborate process and with extreme care. From this material the oxide CeO_2 was obtained perfectly white—a result in corroboration of the researches of Wolf and of Wing, but contrary to later investigators who have always found the substance to be more or less colored. The existence of a white oxide is also confirmed by the recent investigations of Moissan.[1]

The salt chosen for the atomic weight determinations was the sulphate, $Ce_2(SO_4)_3.8Aq$, a compound which is perfectly definite and stable, and which is easily obtained in a state of purity. At 250° it loses its water with facility, and up to 500° it undergoes no further decomposition. By ignition at a white heat, 1500° approximately, all sulphuric acid is expelled, and the pure oxide remains. The other hydrated sulphates of cerium are less manageable. The material studied was derived from three distinct sources, partly from monazite, partly from cerite; and the results attained confirm one another. The weights were as follows, but nothing is said as to their reduction to a vacuum. Probably the reduction was not made.

Hydrous salt.	Anhydrous salt.	CeO_2.
	First Sample.	
1.2385	0.9875	0.5977
1.2730	1.0148	0.6138
1.2030	0.9590	0.5794
1.5420	1.2295	0.7430
	Second Sample.	
0.9642	0.7685	0.4642
1.3260	1.0571	0.6389
1.1429	0.9112	0.5518
0.9072	0.7232	0.4372
	Third Sample.	
1.2114	0.9658	0.5840
1.2411	0.9894	0.5984

From these data the following atomic weights are derived, when $O = 16$ and $S = 32$, cerium being regarded by the authors as a dyad, with the oxide obtained having the formula Ce_3O_4.

[1] *Compt. rend.*, **124**, 1233.

FIRST SERIES.

	From per cent. H_2O.	From "Ce_3O_4" in hydrate.	From Ce_3O_4 in anhydrous salt.
	92.84	93.08	93.16
	92.65	92.88	92.95
	92.65	92.64	92.63
	92.85	92.74	92.70
Mean,	92.74	92.84	92.86

SECOND SERIES.

	92.49	92.55	92.56
	92.69	92.72	92.73
	92.76	93.17	93.30
	92.66	92.77	92.80
Mean,	92.65	92.80	92.85

THIRD SERIES.

	92.75	92.84	92.87
	92.68	92.88	92.93
Mean,	92.71	92.86	92.90
Mean of all,	92.70	92.83	92.87

The extreme variation is 0.75, which becomes 1.125 when cerium is regarded as a triad.

From the entire series of determinations, the salt $Ce_2(SO_4)_3.8Aq$ gives in mean 20.278 per cent. of water, and 48.205 CeO_2. The mean percentage of CeO_2 in the anhydrous sulphate is 60.467. From these data, with $H = 1$, $O = 15.879$, and $S = 31.83$, the following mean values for Ce''' are deduced:

From percentage of water ..... $Ce = 138.14$
From CeO_2 in hydrated salt ..... $Ce = 138.35$
From CeO_2 in $Ce_2(SO_4)_3$ ..... $Ce = 138.42$

The mean of these is $Ce = 138.30$. With $O = 16$, this becomes $Ce = 139.35$.

These figures are adopted in the table at the close of this report, as being probably more trustworthy than the older determinations, but they are still subject to a good deal of uncertainty.

Still another investigation upon cerium is reported by Boudouard,[1] who, following Schutzenberger, fractionates the salts of the metal. His atomic weight determinations are made by ignition of the sulphate; but the values assigned to O and S are

[1] *Compt. rend.*, 125, 772.

not stated. By fractionation of the acetate he gets an oxide giving from Ce = 135.1 to 140.7. From fractionations of the sulphate he finds Ce = 133.0 to 138.75. Hydrogen peroxide precipitates an oxide giving Ce = 137.15 to 137.6, while the unprecipitated portion ranges from 137.85 to 139.9. He concludes that the oxide of cerium is accompanied by small quantities of another earth of lower atomic weight.

Wyrouboff and Verneuil[1] criticise the work of Boudouard, and suggest that his high values for Ce are due to the presence of thoria, while the lower values are ascribable to the other earths of the cerium-yttrium groups. To this criticism Boudouard[2] replies, defending the purity of his material. He now states that his CeO_2 was *white*. Wyrouboff and Verneuil[3] reiterate their objections, and show that the variations in successive portions obtained by Boudouard are irregular, sometimes high, sometimes low, and not systematic in one direction as they should be with material representing an orderly fractionation.

It is evident from the discussion thus summarized that Boudouard's figures relate to mixtures, and not to one earth, whatever the mixtures may be. They are therefore unavailable as determinations of a definite atomic weight. It may be suggested here that a careful scrutiny of the supposed CeO_2 is necessary in order to prove that it is not contaminated by higher or lower oxides of cerium, and that it does not contain, like certain other oxides, occluded gaseous impurities. Until these questions have been settled, all atomic weight determinations based upon weighings of ceric oxide are uncertain.

Gaseous Densities.—Lord Rayleigh[4] has continued his investigation upon the density of the principal gases, and now gives data for CO, CO_2, and N_2O. His results, air being taken as unity, are tabulated as follows:

Oxygen	1.10535
Atmospheric nitrogen, plus argon	0.97209
Nitrogen	0.96737
Argon	1.37752
Carbonic oxide	0.96716
Carbon dioxide	1.52909
Nitrous oxide	1.52951

1 *Compt. rend.*, 125, 950.
2 *Ibid*, 125, 1096.
3 *Ibid*, 125, 1180.
4 *Nature*, December 30, *1897*. *Chem. News*, December 31.

Calculated from the density of CO, with O = 16, C = 11.9989.

Mathematical Relations.—Rummel,[1] in a paper upon "The Spectra of the Alkalies and their Atomic Weights," works out a series of relations which seem to be significant. For the formulae developed, which are algebraic, the original paper must be consulted. When Na = 23, as the starting-point, the spectral relations give He = 3.64, K = 39.05, Rb = 85.15, and Cs = 133.47. These values are near enough to the actual determinations to show that the mathematical process deserves careful consideration.

Miscellaneous Notes.—At the Toronto Meeting of the British Association for the Advancement of Science, Brauner presented a paper on the atomic weight of thorium. Also at the Washington meeting of the American Chemical Society, Venable gave the preliminary results of an investigation upon zirconium. These determinations are as yet unpublished.

A memoir upon the atomic weight of molybdenum, by A. Vandenberghe, has been awarded the Stas prize of the Belgian Academy. It will appear in the quarto form adopted by the Academy for its more important publications.

The following table of atomic weights is essentially that given in Clarke's "Recalculation," a new edition of which was published by the Smithsonian Institution in January. The names of elements which represent changes from the table of 1896 are italicized.

	H = 1.	O = 16.
Aluminum	26.91	27.11
Antimony	119.52	120.43
Argon	?	?
Arsenic	74.44	75.01
Barium	136.39	137.43
Bismuth	206.54	208.11
Boron	10.86	10.95
Bromine	79.34	79.95
Cadmium	111.10	111.95
Calcium	39.76	40.07
Carbon	11.91	12.00
Cerium	138.30	139.35
Cesium	131.89	132.89
Chlorine	35.18	35.45
Chromium	51.74	52.14

[1] *Proc. Roy. Soc.* of Victoria (Australia), 10, Part I, page 75.

	H = 1.	O = 16.
Cobalt	58.55	58.99
Columbium	93.02	93.73
Copper	63.12	63.60
Erbium	165.06	166.32
Fluorine	18.91	19.06
Gadolinium	155.57	156.76
Gallium	69.38	69.91
Germanium	71.93	72.48
Glucinum	9.01	9.08
Gold	195.74	197.23
Helium	?	?
Hydrogen	1.000	1.008
Indium	112.99	113.85
Iodine	125.89	126.85
Iridium	191.66	193.12
Iron	55.60	56.02
Lanthanum	137.59	138.64
Lead	205.36	206.92
Lithium	6.97	7.03
Magnesium	24.10	24.28
Manganese	54.57	54.99
Mercury	198.49	200.00
Molybdenum	95.26	95.99
Neodymium	139.70	140.80
Nickel	58.24	58.69
Nitrogen	13.93	14.04
Osmium	189.55	190.99
Oxygen	15.88	16.00
Palladium	105.56	106.36
Phosphorus	30.79	31.02
Platinum	193.41	194.89
Potassium	38.82	39.11
Praseodymium	142.50	143.60
Rhodium	102.23	103.01
Rubidium	84.78	85.43
Ruthenium	100.91	101.68
Samarium	149.13	150.26
Scandium	43.78	44.12
Selenium	78.42	79.02
Silicon	28.18	28.40
Silver	107.11	107.92
Sodium	22.88	23.05
Strontium	86.95	87.61
Sulphur	31.83	32.07
Tantalum	181.45	182.84

	H = 1.	O = 16.
Tellurium	126.52	127.49
Terbium	158.80	160.00
Thallium	202.61	204.15
Thorium	230.87	232.63
Thulium	169.40	170.70
Tin	118.15	119.05
Titanium	47.79	48.15
Tungsten	183.43	184.83
Uranium	237.77	239.59
Vanadium	50.99	51.38
Ytterbium	171.88	173.19
Yttrium	88.35	89.02
Zinc	64.91	65.41
Zirconium	89.72	90.40

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 26.]

THE VOLUMETRIC DETERMINATION OF COBALT.[1]

By HARRY B. HARRIS.

Received January 14, 1898.

INTRODUCTION.

ZINC, manganese, nickel, and cobalt constitute an analytical group of more than ordinary importance. The methods for the quantitative determination of these metals are mainly gravimetric. The volumetric methods applied in the estimation of zinc have won a permanent place with the analyst, and are used daily, where zinc determinations are of prime interest.

The estimation of manganese by means of potassium permanganate according to the recommendation of Volhard has almost completely supplanted the methods ordinarily used with that metal. When nickel and cobalt are brought to the front, and when the methods proposed at various times for their determination are carefully examined, it will be found that volumetric processes must be relegated to a very subordinate position.

Accurate, rapid, volumetric methods, giving satisfactory results for these two metals, would be welcomed by all analysts. It is true that volumetric methods have from time to time been brought forward, yet they seem not to have met with favor:

[1] From a thesis presented for the degree of Doctor of Philosophy, 1897.

at least they have not gained a permanent hold in the literature pertaining to analysis.

In the hope that perhaps a careful review of some of the proposed schemes for the volumetric determination of cobalt would disclose their inherent weakness with the discovery of modifications which would lead to their elimination and the improvement of the methods, the present investigation was undertaken. The review includes about every method which has been published upon the subject under discussion.

PREPARATION OF MATERIALS.

It seemed advisable not to use the ordinary salts of the market, but to derive the cobalt from some source after careful purification of the same.

To this end, recrystallized, dry, and pure purpureo-cobalt chloride was reduced by means of purified hydrogen in a porcelain crucible. The bright metallic mass after cooling in hydrogen was transferred to a weighing bottle which was preserved in a vacuum desiccator. Portions of this purified metal were weighed off for the several determinations that were made.

REVIEW OF METHODS.

I. WINKLER'S METHOD.

In the *Zeitschrift für analytische Chemie*, **3**, 420, Clemens Winkler called attention to the fact that potassium permanganate will oxidize cobaltous salts; although the precipitation of the cobaltic oxide is not in any sense complete unless there be simultaneously present some substance which will mechanically carry down the cobalt oxide formed.

The reaction was conceived to proceed in the sense of the following equation:

$$6\,CoCl_2 + 5\,HgO + K_2Mn_2O_8 + H_2O =$$
$$3\,Co_2(OH)_6 + 5\,HgCl_2 + 2KCl + 2MnO_2H_2O.$$

The purpose of the mercuric oxide is merely to mechanically separate the cobaltic oxide from the solution. The method seemed to be, in the main, very satisfactory.

As indicated in the equation, the salt used was the chloride. The oxidation is retarded by sulphuric acid, while even traces of other oxy-acids prevent it. The presence of organic sub-

stances is harmful, but ferric salts are without influence.

So far as can be determined from the various papers by Winkler upon this method, he operated in the cold. No mention is made of this point, although the succeeding work will prove that it is a matter of moment.

Indeed, it was observed when operating in the cold that when the point of complete oxidation was approached the solution frequently acquired a muddy appearance, and that the action of the permanganate was decidedly sluggish, consequently the end of the reaction was noted with difficulty.

In *hot* solutions, on the contrary, the end reaction was comparatively sharp and the pink color observed without great effort. In the trials made, the solution of the chloride was brought to boiling ; the mercuric oxide was then introduced and the permanganate added, with frequent shaking of the containing flask. The precipitated mercuric oxide was found to be the most suitable, it being more efficient in the precipitation of the cobaltic oxide.

The mercuric oxide was preserved, according to the recommendation of Winkler, as an emulsion, and was so added as occasion demanded. Experience demonstrated that when the cobalt content of the solution was high, it was advisable to dilute it with water to one-half or even more. This facilitated and made more certain the reading of the end reaction. The permanganate usually consisted of about four grams of the pure salt dissolved in one liter of water. A solution of cobalt as chloride, containing 0.1334 gram, was first used.

When the analysis was conducted as outlined above, the following results were obtained :

	Gram.	Per cent.
1	0.1332	99.85
2	0.1329	99.62
3	0.1323	99.17
4	0.1332	99.85
5	0.1338	100.30

These determinations were made in boiling solutions, and confirm the statement that in the cold the reaction is so slow that its conclusion cannot be sharply determined.

To verify this, the results which were gotten when operating

in the cold are introduced, the solution used containing 0.1334 gram cobalt as the chloride:

	Gram.	Per cent.
1	0.1253	93.93
2	0.1253	93.93
3	0.1244	93.25
4	0.1241	93.03

The cobalt content of the solution was reduced and a series of oxidations carried out in the same manner as before, observing every precaution.

With a cobalt solution of 0.0534 gram operating in *hot solution* the results were:

	Gram.	Per cent.
1	0.0527	98.67
2	0.0529	99.05
3	0.0518	97.00
4	0.0536	100.38
5	0.0533	99.81

while in the cold there was obtained:

	Gram.	Per cent.
1	0.0503	94.11
2	0.0503	94.11
3	0.0501	93.71
4	0 0491	91.83

The cobalt content was now increased to 0.2668 gram with the following result in *hot* solution:

	Gram.	Per cent.
1	0.2649	99.31
2	0.2646	99.21
3	0.2639	98.94

In *cold* solution:

	Gram.	Per cent.
1	0.2375	89.02
2	0.2357	88.36
3	0.2369	88.80

Two facts are obvious in these results, the method is satisfactory and yields concordant percentage when it is carried out in hot solutions. It is also apparent that, as the quantity of cobalt is raised, the results do not approach the theoretical so closely.

As previously observed, the mercuric oxide was found efficacious in withdrawing the cobaltic oxide from solution. Other

reagents designed to perform the same function were tried ; thus, in using barium carbonate with a solution of 0.1334 gram cobalt, low end readings were obtained.

	Gram.	Per cent.
1	0.0989	74.14
2	0.0972	72.93
3	0.0936	70.16

Ferric hydroxide was also applied, but it proved worthless.

In the well-known method of Volhard for the determination of manganese by means of potassium permanganate, zinc sulphate is added. With the cobalt salt this was without effect, and evidently for the reason that the action of the permanganate in the case of manganous and cobaltous salts is quite different.

In the first case there is formed an oxide of decidedly acidic character which tends to combine with oxides still present in the solution, and for this the zinc salt is well suited. Whereas in the cobalt salt the oxidation proceeds with the formation of a rather indifferent sesquioxide which must be mechanically carried down.

On using an emulsion of zinc oxide, the oxidation with potassium permanganate proceeded very slowly, the liquid also clarifying with difficulty.

However, on adding to the solution of cobalt chloride, containing zinc oxide, a solution of ferric chloride, the titrations advanced rapidly in hot solutions, and the cobaltic oxide settled out quickly ; this was no doubt due to the influence of the ferric hydroxide. As evidence of the value of the above procedure, the following results are appended :

	Theoretical cobalt. Gram.	Found cobalt. Gram.	Percentage.
1	0.1334	0.1330	99.70
2	0.1334	0.1328	99.55
3	0.1334	0.1332	99.85
4	0.1334	0.1336	100.15
5	0.1334	0.1363	99.50
6	0.1334	0.1363	99.50
7	0.1334	0.1369	99.93
8	0.1334	0.1362	99.42

Cobalt is quite frequently associated in minerals and ores with arsenic as well as with nickel. By the usual method of solution of such compounds, the arsenic, for example, would be

brought into the state of arsenic acid, and when in this condition it prevents the oxidation of the cobalt; when nickel is present it was thought that, by means of a double titration in presence of arsenic acid, the cobalt might be determined, but experiment proved the contrary.

Not infrequently copper is found associated with cobalt. How its presence would influence the determination of the latter by the method under discussion seemed of interest, and experiments with this end in view were instituted. The first solution operated upon contained 0.1370 gram of cobalt and 0.0125 gram of copper, and gave upon titration:

	Cobalt. Gram.	Per cent.
1	0.1363	99.49
2	0.1360	99.28
3	0.1359	99.18

When the copper content was raised to 0.0500 gram, the cobalt found was

	Cobalt. Gram.	Per cent.
1	0.1365	99.64
2	0.1362	99.42
3	0.1360	99.28

But on raising the copper to 0.1300 while the solution still contained 0.1370 gram cobalt there was found:

	Gram.	Per cent.
1	0.0804	58.69
2	0.0783	57.15
3	0.0795	58.03

Recalling the fact that when ferric chloride was added to a solution of cobaltous chloride containing zinc oxide, the hitherto murky solution became clear, and allowed of a complete oxidation of the cobalt, the thought suggested itself that possibly the oxidation of cobalt salts in the presence of mercuric oxide would be complete in the cold, if ferric chloride was added, but experiment did not bear out the suggestion. 0.1370 gram of cobalt gave:

	Gram.	Per cent.
1	0.1331	97.16
2	0.1329	97.01
3	0.1335	97.45

Lead is another metal which sometimes occurs associated with cobalt. In solutions of cobalt and lead the cobaltic oxide was almost quantitatively precipitated by potassium permanganate on addition of mercuric oxide and ferric chloride. A solution containing 0.1370 gram cobalt and 0.0120 gram of lead gave :

	Cobalt. Gram.	Per cent.
1	0.1372	100.15
2	0.1369	99.93
3	0.1373	100.22

As the lead content is raised the results depart from the theoretical quite considerably.

In the presence of arsenic acid and ferric chloride the titration of cobalt can be made by means of potassium permanganate, using mercuric oxide to carry down the cobaltic oxide. With these conditions a cobalt solution of 0.1272 gram gave :

	Cobalt. Gram.	Per cent.
1	0.1273	100.08
2	0.1268	99.70
3	0.1270	99.84

With antimony the remarkable observation was made that as the content of this metal was increased the determination of the cobalt became exact. A solution containing 0.1272 gram cobalt and 0.0900 gram of antimony gave on titration :

	Cobalt. Gram.	Per cent.
1	0.1323	104.01
2	0.1317	103.54
3	0.1321	103.85

When the antimony was raised to 0.1700, while the cobalt content remained the same, the solution gave on titration :

	Cobalt. Gram.	Per cent.
1	0.1297	101.97
2	0.1289	101.33
3	0.1304	102.52

But when 0.4400 gram antimony were present with 0.1272 gram of cobalt the results obtained were :

	Cobalt. Gram.	Per cent.
1	0.1274	100.16
2	0.1265	99.45
3	0.1267	99.60

In this review of Winkler's method the conclusions reached are that the results are fairly accurate when the cobalt content is not too great, but that it can scarcely claim recognition as a trustworthy method under most conditions, and that it can in no wise be regarded as equal in value to the ordinary gravimetric methods employed in the estimation of this metal.

Winkler has asserted in the *Zeitschrift für analytische Chemie*, **7**, 48, that the method is applicable in the analysis of a speiss holding arsenic and nickel, yet his own results seem to show that the conditions must be accurately known, otherwise the method is faulty.

Work done with these conditions shows that the determinations were least unsatisfactory when the cobalt stood to the nickel in the ratio of 1 : 2; but even then the results were always high.

II. MCCULLOCH'S METHOD.

This method appeared in the *Chemical News*, Vol. **59**, and, for its execution, requires the following salts for its execution: Potassium bichromate, ferrous ammonium sulphate, and a solution of potassium cyanide. In carrying out the method, the solutions of bichromate and potassium cyanide are brought together in a flask, the mouth of which is closed with a doubly perforated cork fitted with a thistle tube and an exit tube. A few drops of ammonia are added to the solution to neutralize any free acid which may be present, after which the liquid is boiled to expel the air from the flask.

There is next added the solution under examination, which must be hot, then the reaction occurs almost instantaneously and is complete. The cork carrying the thistle tube is no longer necessary.

An excess of a warm concentrated solution of ammonium chloride is now added and the whole boiled for a short time to drive off the excess of potassium cyanide. Nickel sulphate is now added and the cobaltic cyanide is precipitated.

The nickel sulphate also serves to decompose the potassium nickel cyanide which otherwise would combine with the ferrous ammonium sulphate subsequently introduced, with the consequent production of low results. The solution so precipitated is brought together with a known quantity of ferrous ammonium sulphate and after the addition of a few drops of hydrochloric acid it is titrated with potassium bichromate of known strength.

A solution of 0.1144 gram of cobalt when titrated as above, gave with these conditions (25 cc. potassium cyanide and 25 cc. potassium bichromate):

	Cobalt. Gram.	Per cent.
1	0.1032	90.21
2	0.1039	90.82
3	0.1014	88.64
4	0.1000	87.41
5	0.1023	89.42

When the quantity of potassium cyanide was reduced one half, the results obtained were:

	Cobalt. Gram.	Per cent.
1	0.1056	92.32
2	0.1030	90.04
3	0.1000	87.41
4	0.1060	92.67
5	0.1022	89.32
6	0.1004	87.85
7	0.1009	88.20
8	0.1022	89.32
9	0.1015	88.72
10	0.1020	89.15
11	0.0995	86.97

From this series of results, obtained with the exercise of great care, it is obvious that the suggestion of McCulloch possesses little merit in the desired direction.

The wide divergence of these results from the theoretical and from each other, show that the method has defects.

III. FLEISCHER'S METHOD.

In the *Journal für praktische Chemie*, **110**, 49, there is published by E. Fleischer a method intended for the separation of cobalt from nickel, and the subsequent volumetric determination of the separated cobaltic oxide.

The cobalt salt under examination is mixed with an excess of sodium hydroxide and then treated with a solution of sodium hypochlorite.

Both of these reagents are added in excess, as the complete oxidation of the two metals is of primary importance. The solution is brought to a boil and the black precipitate, consisting of the two sesquioxides, after settling, is filtered off and is then treated with a solution of ammonia (1 : 3).

On applying heat the nickelic oxide is reduced completely, leaving the cobaltic oxide unchanged; this is filtered off and brought in contact with ferrous ammonium sulphate and sulphuric acid, when the ferrous salt will be oxidized at the expense of the cobaltic oxide.

The unchanged ferrous salt is then determined by titration with potassium permanganate.

On working with a solution containing 0.1240 gram cobalt and 0.1263 gram nickel, the resulting sesquioxides were treated with dilute ammonia and boiled for a short period; it was then filtered and treated with ferrous ammonium sulphate and titrated as recommended, with the result that there was found:

	Cobalt. Gram.	Per cent.
1	0.1730	139.52
2	0.1730	139.52
3	0.1729	139.44
4	0.1730	139.52

With 0.0496 gram cobalt and 0.1263 gram nickel, following the method with care, I found:

	Cobalt. Gram.	Per cent.
1	0.0620	125.00
2	0.0619	124.86
3	0.0627	125.98
4	0.0651	131.25

With 0.1240 gram cobalt and 0.0506 gram nickel, there resulted:

	Cobalt. Gram.	Per cent.
1	0.1407	113.47
2	0.1400	112.90
3	0.1350	108.07
4	0.1384	111.61

But, on making up an ammoniacal solution of ammonia (sp. gr. 0.96), with three parts water, as recommended, and boiling for a longer period, the results were more concordant.

With a solution containing 0.0915 gram cobalt and 0.1263 gram nickel, there was found :

	Cobalt. Gram.	Per cent.
1	0.0935	102.19
2	0.0937	102.51

On lowering the nickel content to 0.0550 gram and submitting the oxides to the action of boiling ammonia for one hour, the results continued high.

	Cobalt. Gram.	Per cent.
1	0.1097	119.89
2	0.1094	119.56

When the period of boiling was extended to two hours, 0.0915 gram cobalt, in the presence of 0.1263 gram nickel, gave :

	Cobalt. Gram.	Per cent.
1	0.0937	102.62
2	0.0930	101.64

But when the nickel content was lowered to 0.0505 gram and the solution was boiled for two hours, the results were high :

	Cobalt. Gram.	Per cent.
1	0.1048	114.53
2	0.1035	113.11

These results show conclusively that the weakness of the method is in the reduction with ammonia. The proportion of the two metals is also shown to have an effect on the determination : the proportion of 2 cobalt to 1 nickel seemed especially unfavorable.

IV. DONATH'S METHOD.

In the *Berichte, 1879*, p. 1868, appears a method devised by Donath. It is really proposed as a modification of the Fleischer method. The instability of the sodium hypochlorite is a bar to its general acceptance, as is also the reduction by ammonia.

As a modification, Donath suggests the oxidation by iodine in a sodium hydrate solution, whereby the cobalt is completely converted into the sesquioxide state, while the nickel remains as

nickelous oxide. The precipitate may then be filtered off and the sesquioxide brought into a distilling apparatus along with hydrochloric acid, when the following reaction takes place :

$$Co_2O_3 + 6\ HCl = CoCl_2 + 3\ H_2O + Cl_2.$$

The liberated chlorine is conducted into a potassium iodide solution and the liberated iodine is titrated by sodium hyposulphite.

From the iodine found the cobalt can be readily calculated.

On oxidizing a solution containing 0.1263 gram nickel and 0.1240 gram cobalt with thrice sublimed iodine, the results were always high, as the following series will show :

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1	0.1240	0.1414	114.03
2	0.1240	0.1426	115.00
3	0.1240	0.1286	103.71
4	0.1240	0.1240	100.00
5	0.1240	0.1438	115.97
6	0.1240	0.1388	111.93
7	0.1240	0.1607	129.60

But on using chemically pure iodine the results were much closer :

	Cobalt. Gram.	Gram.	Per cent.
1	0.1240	0.1261	101.69
2	0.1240	0.1240	100.00
3	0.1240	0.1235	99.60
4	0.1240	0.1296	102.34
5	0.0496	0.0480	96.57
6	0.0496	0.0491	98.99
7	0.0496	0.0478	96.16
8	0.0496	0.0500	100.81

When the nickel content was reduced to 0.0506 gram with 0.1240 gram cobalt, the results were as follows :

	Cobalt. Gram.	Gram.	Per cent.
1	0.1240	0.1243	100.24
2	0.1240	0.1248	100.65
3	0.1240	0.1236	99.76
4	0.1240	0.1251	100.88

From these results it can be seen that the purity of the iodine is of prime importance, otherwise part of the nickel will be oxidized. The method may be considered as fairly accurate.

V. VON REIS' METHOD.

In the *Zeitschrift für angewandte Chemie, 1890*, appears an article by M. A. von Reis and F. Wiggert on the determination of cobalt in the volumetric way.

The cobalt solution is treated with an emulsion of zinc oxide and brought to boiling, when a known quantity of a standardized solution of potassium permanganate is added.

The oxidized cobalt falls to the bottom and allows of the back-titration of the potassium permanganate by ferrous ammonium sulphate.

	Cobalt present. Gram.	Cobalt found. Gram.	Percentage.
1	0.1334	0.1330	99.70
2	0.1334	0.1325	99.32
3	0.1334	0.1328	99.55
4	0.1334	0.1334	100.00
5	0.1334	0.1340	100.45

To all appearances this is by far the most satisfactory method yet proposed. Its simplicity recommends it.

CONCLUSION.

After careful repetition of these methods, making varying conditions wherever deemed advisable, one is justified in concluding that none of them possess the degree of accuracy required in any trustworthy determination of cobalt. A good volumetric method for this purpose still remains to be devised.

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RECENT WORK IN ENGLAND ON THE PURIFICATION OF SEWAGE.[1]

By LEONARD P. KINNICUTT.

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THERE are few questions connected with municipal government which cause as much trouble as the disposal of sewage in such a manner as to prevent any cause for complaint, and it is certainly not far from the truth to say that, at the present time, there is no large inland city in the world that has succeeded in satisfactorily disposing of the refuse matter that passes through the sewers.

[1] Read at the Washington Meeting, December 29, 1897.

The three methods used for the purification of sewage are: irrigation, or sewage farming; chemical precipitation; and intermittent filtration.

The first two methods have been tried by many large cities, and opinions differ as to their comparative merits. The history of sewage disposal is evidence of this difference of opinion.

There are in Great Britain forty-three cities which have a population of over 70,000. Direct information from personal investigation shows that, in 1897, twenty-one of these cities discharged their sewage practically untreated into tidal rivers, or into the sea: Liverpool, Edinburgh, Dublin, Belfast, Bristol, Newcastle, Hull, Portsmouth, Dundee, Cardiff, Oldham, Sunderland, Aberdeen, Brighton, Birkenhead, Swansea, Gateshead, Plymouth, South Shields, Middleborough, Cork, and Stockport; nine used chemical precipitation as a means of purification: London, Glasgow, Leeds, Sheffield, Bradford, Salford, Bolton, Huddesfield, and Southampton; two, chemical precipitation, allowing the effluent to pass over a small area of land: Manchester, 30 acres, and Burmley, 30 acres; five, broad irrigation: Leicester, Blackburn, Norwich, Preston, and Walsall; two, broad irrigation preceded by chemical precipitation: Birmingham and Wolverhampton; one used chemical precipitation for a portion of the sewage and broad irrigation for the remainder: Rochdale, chemical precipitation with 250,000 gallons and broad irrigation with 1,000,000 gallons. Of the German cities containing over 70,000 inhabitants, only Berlin, Breslau, Madgeburg, Frankfort, Danzig, Charlottenburg, Braunschweig, Halle, and Essen treat the sewage. Frankfort, Halle, and Essen by chemical precipitation, the other cities by broad irrigation, Berlin using for the purpose 14,473 acres and having in reserve 6,737 acres.

In all these cities there is great difficulty in obtaining satisfactory results. Those cities using broad irrigation find that more and more land must be added to the so-called sewage farm to prevent the drainage from causing a nuisance, and in those cities where the chemical precipitation method is employed, there is no doubt that there has been great difficulty in obtaining sufficient purification, especially when the surrounding district is extensively occupied, and where there is no large watercourse to carry away the purified effluent. The question, there-

fore, that is now engaging the attention of sanitary engineers is, can that third process, intermittent filtration, be substituted in place of the other two?

The work that has been carried on at the Lawrence Experiment Station in regard to this third method of purification, is too well-known to all interested in the subject for me to dwell upon it, and I think it is only necessary to state that the experiments there carried out have shown that 100,000 gallons of crude sewage per day can be purified in the spring, summer, and autumn months by allowing it to filter through one acre of prepared sand filter-beds, underdrained at a depth of from three to five feet. In winter, however, where the filter-beds are unprotected from frost, snow, and ice, according to my observations, very much more than one acre of land is required for each 100,000 gallons. The top layer of sand becomes covered with a layer of what might be called *papier-mâché*, varying from one-eighth of an inch to almost a half inch in thickness. The formation of this layer is due to the finely divided paper in the sewage, and it is almost impervious to water. During the warm months, this coating is prevented from forming, by raking over the surface of the beds each week or two, but between the middle of November till the last of March in the cities of Massachusetts, this cannot be done and, as a rule, they are left untouched during this time. The rate of filtration gradually grows less and less, and from what I have seen at Gardner, Marlboro, Brockton, Framingham, and Westboro, I believe that twice, at least, and possibly four times as much area is required in winter as in summer.

This is a most serious defect in the process of intermittent filtration as recommended by the State Board of Health, of Massachusetts, and any improvement in the process which will partially obviate or remove this difficulty, either by reducing the amount of filtering surface required, so that covered beds could be used, or by preventing the finely ground paper from coming in contact with the filter-beds, so that the *papier-mâché* coating would not form, would be of great value. Such being the case I have been much interested in the recent developments in sewage treatment made in England, especially in the work of Dibden's bacteria filter now in use at Sutton, and in Cam-

eron's septic tank, now being tried at Exeter. Before speaking of these methods, however, I would like to say a word in regard to the filtering material used in Great Britain. Here sand is almost universally employed, there, on account of the difficulty of procuring sand of the desired quality, various other substances have been tried, burnt clay, or clay ballast, coke, breeze, cinders, clinkers, finely divided coal, etc., and it has been found that any jagged, porous substance is well fitted for the purpose, though curiously enough, experiments seem to show that either fine coal or fine cinders, are, on the whole, the best.

Regarding the special work that I have mentioned, Dibden's bacteria is the outcome of experiments made at Barking on the effluent of London sewage, the sewage itself being chemically treated with lime and iron sulphate.

In making the filtering at Barking the drains had been so arranged that by closing the valve of the main underdrain, the sewage could be kept in the bed for any number of hours, and a series of experiments were made with the view of ascertaining what would be the result of allowing the sewage to remain in the filter for a varying number of hours before passing it into the underdrains, the idea being that the work of purification was not limited to the surface, but took place throughout the body of the filter, and that a greater amount of purification could be obtained by filling the filter and allowing it to stand full for a certain length of time, thus giving the micro-organisms in the center and at the bottom of the bed the same amount of work to do as those nearer the surface, than by allowing the sewage merely to drain slowly through it. The method of working the bed was as follows:

The underdrains being closed, the filter was filled with dilute sewage which was allowed to remain in it for two hours; the drains then being opened, the purified sewage was allowed to run off, air being drawn into the filter as the effluent ran out, the whole cycle requiring seven hours. The filling, standing, and emptying was constantly repeated for six days, when the work was stopped for twenty-four hours to allow of further aeration. The results obtained were most satisfactory. Running at the rate of 500,000 gallons per day, the albuminoid ammonia

was reduced from 0.712 part in 100,000 to 0.162, showing a purification equal to seventy-eight per cent. Running at the rate of 1,000,000 gallons per day, the purification, measured in the same way, equaled sixty-six per cent.

When both the amount treated and the percentage of purification are taken into account, this result is surprisingly good; yet the chief difference between these experiments and those that had been previously made, was that the whole of the filtering material was brought into intimate contact with the organic substance of the dilute sewage and allowed to remain in contact with it for a definite time, thus making full use of the cubical capacity of the filter.

The use in this way of the whole cubical capacity of the filter was new, and although it is only three years since these experiments were made, many sanitary engineers now claim that the cubical capacity of a filter should be taken into consideration in determining its purifying power and not only its superficial area, as has been the case. Therefore, instead of saying that one acre of filtering material three feet deep is capable of purifying so many hundred thousand gallons of sewage, one should say that the purification could be accomplished by 130,680 cubic feet of filtering material. Taking into account the depth of the filter as well as its area, is most important, for it leads to the possibility of purifying large amounts of sewage on comparatively small areas. The depth of the filter, however, must necessarily be limited to the point to which the air can be carried down in sufficient quantities for successful aeration, and as yet a sufficient number of experiments have not been made to decide how deep air can thus be carried, though undoubtedly the depth will be found to depend more or less on the filtering material that is used.

Sutton is the first town to attempt purifying its crude sewage by the above method, and as the plant is under the direction of Mr. Dibden and Mr. Thudicum, a detailed description of the filter and the results obtained, gathered by a personal visit to the works, may be of interest.

The population draining into the sewers is about 13,000, and the dry weather flow equals about 400,000 gallons per day. The sewage system is on the "separate" plan, rainfall being excluded,

yet during wet weather a large volume of subsoil water gains access to the sewers. The town contains few, if any, manufacturing establishments, and the sewage may be considered as a strong domestic sewage.

Sutton formerly purified its sewage by the use of chemicals and one of the precipitating tanks was utilized for the construction of a filter. On the floor of the tank, whose area was 183 square yards, was laid a six-inch drain, connected with nineteen lateral drains three inches in diameter. The main drain was provided with a six-inch valve so that the filter could be emptied or filled at will. The pipes were covered with very coarse, burnt clay, and upon this was placed a layer of burnt clay three feet deep, the smallest pieces of which could not pass through a half-inch mesh. The total capacity of this filter was 218 cubic yards, and when filled with burnt clay it would hold 13,500 gallons.

The crude sewage, after passing through iron screens to intercept large pieces of paper, is carried directly to the filter, the flow being stopped as soon as the sewage level reaches within an inch or so of the burnt clay. The time required for filling the filter is about one hour. The filter is allowed to remain full for about two hours, and then emptied, the time occupied in emptying it being one and one-half hours. The filter is then allowed to rest for two hours after which it is again charged. The effluent obtained is clear and without any strong odor, and appears to the eye equal to the best effluent obtained by the chemical precipitation process. From analyses made three or four times each month, from November, 1896, to June, 1897, and published in the *Surveyor* for July 9, 1897, the amount of purification as calculated from the albuminoid ammonia equals about fifty-eight per cent., while the amount of suspended matter is reduced from fifty to two and three-tenths grains per gallon.

The work of the filter compares favorably with the results obtained by many of the chemical precipitation processes, and, though twelve months is possibly too short a period from which to draw conclusions, the city is now constructing three more bacteria filters, and there seems to be no question that the above method leads one to entertain the view that with domestic sewage a purification equal to that obtained by chemical pre-

cipitation is possible with comparatively small, artificially prepared filters; and from experiments which are now being made, it seems possible that some similar plan can be used with the sewage of a manufacturing city.

The effluent obtained by the bacteria filter when running at the rate of 1,000,000 gallons per acre, is not sufficiently pure to drain into a water-course, whose volume only equals or is less than the volume of the effluent, and when the stream runs through a thickly populated district as is the case in Sutton, and, consequently, there the first effluent is run through another filter of the same size and construction, filled however with burnt clay, all of which is small enough to pass through a half-inch mesh. The effluent from this second filter, at the time of my visit, was bright, clear, and without odor. The average amount of albuminoid ammonia in this effluent during the seven months from November to June was 0.243 part in 100,000 parts, the original sewage containing 1,130 parts, and the amount of suspended matter was reduced to 0.703 grain per gallon.

These results are certainly most interesting and instructive, and show what advance is being made in the process of purifying sewage by means of those micro-organisms which fulfil their life-functions in the presence of oxygen. Still more interesting than the bacteria filter on account of its being an entirely new departure, is the septic tank system of purification introduced by Donald Cameron, of Exeter, England. It has long been known that in the decomposition of organic matter by micro-organisms not a single species, but many species are at work and that they could roughly be divided into two classes: the putrefactive bacteria, those which live in the absence of light and oxygen and exercise a reducing or deoxidizing action, and those organisms whose life depends on the presence of oxygen and are known as the nitrifying bacteria. Mr. Cameron's septic tank treatment is based on the idea that the decomposition of organic matter is more easily and rapidly accomplished if the deoxidizing bacteria are allowed to do their work before the organic matter comes in contact with the nitrifying organisms. This is, of course, contrary to the commonly accepted idea that sewage is best treated before putrefaction begins, yet there is much to be said in favor of Mr. Cameron's plan. To separate the two

kinds of action the sewage is first led into a large tank, vaulted so as to exclude light and air, and is allowed to remain in this tank till putrefaction has taken place, when the sewage is passed upon the filter-beds which contain, as all filter-beds do, the nitrifying organisms. This method of treatment has been introduced into Exeter, England, and at present about 70,000 gallons are being treated each day.

The plant consists of the so-called septic tank, which is an underground tank built of cement concrete, sixty-four feet long, eighteen feet wide, and of an average depth of seven feet, having a capacity of about 53,000 gallons and of five filters made of coke breeze and furnace clinkers, about five feet in depth and covering all together an area of 400 square yards, having a capacity of 695 cubic yards. The crude sewage as it arrives at the plant passes through a railing to prevent large objects from entering the tank, while all small particles and solids in suspension pass freely to a grit chamber which is divided in two, each part having an inlet into the tank. The inlets are close to the bottom of the tank and the aperture of the inlet pipes is smaller on the tank side than on the sewer side, so that the sewage enters the tank with considerable force. The outlets are also beneath the surface of the water so as not to admit air or light, and so arranged that the water at the middle depth alone escapes. They are gauged so that the rate of flow may be measured; usually it is about 3,000 gallons per hour. The sewage from the septic tank is discharged simultaneously on two of the bacteria filters arranged according to Dibden's method. When these two filters are full they are emptied of their contents, and, while being emptied, the sewage from the tank passes on to others. The fifth filter remains idle one week, when it takes the place of the one that has longest been in use. Thus each filter remains idle one week out of every four. The filling and emptying of these filters is done automatically by an ingenious arrangement patented by Mr. Cameron and is said to be most satisfactory.

The action inside the tank is essentially of a putrefactive nature, no nitrates being formed. The organic matter is decomposed, or rather broken up into simpler forms, a large amount being rendered soluble, while at the same time ammonia and, I believe, free nitrogen are being formed. According to analyses

made by Dibden, the amount of oxidizable organic matter in solution is reduced about 30.8 per cent., the free ammonia about 26.9 per cent., the albuminoid ammonia about 17 per cent., and the suspended solids about 55 per cent. Pearmain and Moor, who have made a report on the process, state that there is no accumulation of sludge in the tank beyond a small amount of thin black sediment, which they report is so slight that a year's accumulation would scarcely be worth the trouble of removing. F. J. Commin, in a report on the process published in the *Lancet* for December, *1896*, says that the deposit is very fine and inorganic, and that in a small tank after seven months' continual working and after quite 2,000,000 gallons of sewage had passed through the tank, the deposit was less than four inches over a surface of twenty-four feet by nine feet.

On top of the liquid in the tank there is a layer of flocculent matter from two to two and one-half inches in thickness, and from all accounts this seems to have been formed during the first few weeks that the tank was used and not to have increased much in thickness since that time. It appears to be composed of organic matter, formed I believe from the suspended matter in the sewage, and from all the information I have been able to obtain, it seems as though the organic matter in this flocculent layer was at first partially decomposed by the putrefactive organisms. Portions of it then sank to the bottom of the tank, where further action took place. Bubbles of gas collected around the fragments that had been carried down, causing them to rise to the surface and this process went on till the residue that remained at the bottom contained very little organic decomposable matter.

This action reminds one of what takes place in small streams into which sewage is emptied. I have often seen in such streams cakes of at least one-half yard in circumference rise from the mud at the bottom, and float down with the current.

According to Dibden the liquid that comes from the tank is of a brownish yellow color, offensive, and contains 2.73 grains per gallon of free ammonia, 0.175 grain of albuminoid ammonia, and the amount of oxygen absorbed from potassium permanganate in four hours is 1.405 grains per gallon. It contains no nitrates nor nitrites. The original sewage contained at the

same time 3.778 grains free ammonia, 0.212 grain albuminoid ammonia, and the oxygen absorbed from the potassium permanganate was 2.028 grains per gallon. This liquid is passed upon the filters as has been described and the effluent from these filters contains 1.705 grains free ammonia, 0.078 grain albuminoid ammonia, 0.253 grain nitrogen as nitrites, 0.353 grain nitrogen as nitrates, no suspended matter, and the absorbed oxygen from the potassium permanganate in four hours is only 0.388 grain per gallon.

The great advantage of the septic tank process, if it does what it appears to do, is that so large an amount of suspended matter is removed from the sewage that there will be very much less trouble with the clogging up of the surface of filter-beds in winter, and consequently an area that is large enough for the purification in summer will be more nearly, or possibly quite, sufficient for the work during the winter months.

It is also claimed that a large amount of the organic matter in solution is removed in the septic tank and if this is so, which appears probable from the analyses that have been made, it may not be too much to hope that future developments in this direction taken in connection with the using of the cubical capacity of a bacteria filter, may so reduce the area required for purification, that filter-beds may, without too great expense, be protected from snow and ice.

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INVESTIGATION OF THE THEORY OF SOLUBILITY EFFECT IN THE CASE OF TRI-IONIC SALTS.

By ARTHUR A. NOYES AND E. HAROLD WOODWORTH.

Received January 20, 1898.

THE theory of the effect of salts on the solubility of one another has, in the case of di-ionic salts having one ion in common, been quite thoroughly tested and confirmed.[1] The solubility of tri-ionic salts in the presence of other salts, however, has been much less investigated. The theory of the phenomenon has, to be sure, been already developed, and has been partially tested by experiments with lead chloride in the presence of other salts.[2]

[1] Compare especially Noyes and Abbot: *Ztschr. phys. Chem.*, 16, 125.

[2] Noyes: *Ibid.*, 9, 626.

There was found, however, to be only an approximate agreement between the theory and the facts, probably because the dissociation-values involved are uncertain. Moreover, the theory could not be tested in the case where a salt with a common bivalent ion was added, probably owing to the fact that a double salt was formed. A further investigation of the subject seems therefore to be desirable.

To this end we have determined the solubility of lead iodide in pure water, and in potassium iodide and lead nitrate solutions of varying strengths. We made use of lead iodide because of its slight solubility (one molecular weight in about 600 liters); for, in such dilute solutions, the influence of the two substances on the dissociation of one another is hardly appreciable, and the tendency to the formation of double salts is ordinarily very slight,—two phenomena which often have a disturbing influence in concentrated solutions. In order to determine the solubility, we have measured the electrical conductivity of the saturated solutions, and subtracted from it the conductivity of the water or of the solutions before treating with lead iodide. This method has the advantage over the analytical determination, of greater convenience; and in this case it is especially well adapted, as it furnishes directly a knowledge of the concentration of the ions, so that it is not necessary to consider dissociation-values.

Two samples of each of the three salts were prepared by different methods. These samples were in all cases shown to be exactly alike as far as the conductivity of their solutions was concerned, which indicates that the substances were, in all probability, pure. One sample of the potassium iodide was prepared by treating the commercial, chemically pure salt with alcohol until it was about one-half dissolved, and by subsequent crystallization from this solution by evaporation. The other sample was obtained by crystallizing from water, the residue left undissolved by the alcohol. The lead nitrate was in one case obtained by crystallization of a commercial sample from water; in the other, by precipitation with nitric acid followed by crystallization from water. One sample of lead iodide was prepared by metathesis from lead acetate and potassium iodide; the other, by dissolving a commercial preparation in a strong potassium iodide solution, and then diluting with water. In

both cases the salt was purified by crystallizing twice from water. The solubility determinations were carried out as follows: Small forty-cc. glass-stoppered bottles were charged with an excess of the solid lead iodide and with pure water or with solutions of lead nitrate or potassium iodide; the stoppers were coated with paraffin, and the bottles rotated for five hours in a thermostat by means of a previously described apparatus.[1] The solutions were then allowed to settle for a short time, and blown out by means of a wash-bottle arrangement into a resistance cell of the Arrhenius type; and the conductivity was measured in the usual way.[2] All the solubility determinations and conductivity measurements were carried out at 25°. In all cases, duplicate determinations of the solubility were made in such a way that the condition of saturation was approached from both sides—that of supersaturation and that of undersaturation. Moreover, in order to make certain of the purity of the lead iodide, not only were the two different samples used, but each sample was also treated with successive amounts of water, and the conductivity of the corresponding solutions determined. A complete agreement was found to exist.

The following tables contain the specific conductivities (multiplied by 10^{-7}) expressed in Siemens' units. In all cases the conductivity of the water used (which was equal to 9×10^{-7}) has been subtracted.

CONDUCTIVITY OF WATER SATURATED WITH LEAD IODIDE.

	I.	II.	III.	IV.	Mean.
Undersaturated....	4016	4016	4023	4030	4021
Supersaturated....	4039	4041	4042	4041	4041

CONDUCTIVITY OF POTASSIUM IODIDE SOLUTIONS SATURATED WITH LEAD IODIDE.

Concentration of the potassium iodide	=0.003077 equivalent per liter.		0.002000 equivalent per liter.	
	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
I.....	6174	6184	5316	5343
II.....	6172	6200	5310	5335
Mean.....	6173	6192	5313	5339

[1] *Ztschr. phys. Chem.*, 9, 606.

[2] Ostwald: *Ztschr. phys. Chem.*, 2, 561.

CONDUCTIVITY OF LEAD NITRATE SOLUTIONS SATURATED WITH LEAD IODIDE.

Concentration of the lead nitrate	=0.003077 equivalent per liter.		0.002000 equivalent per liter.	
	Undersaturated.	Supersaturated.	Undersaturated.	Supersaturated.
I	6807	6783	5798	5800
II	6791	6799	5796	5784
III	6799	6802	....	....
Mean	6799	6795	5797	5792

A consideration of the results in the tables shows that the comparable values agree closely with one another, although the determinations were carried out with different salts and at different times. The supersaturated solutions were, to be sure, about a half per cent. higher than the undersaturated, except in those experiments where lead nitrate was used, in which case they were practically equal. In the calculations described below, of the corresponding concentrations of the ions, the mean of the supersaturated and of the undersaturated values is always used.

In the following tables, the specific conductivities of the pure potassium iodide and lead nitrate solutions are given. In the upper half are the conductivities of the freshly-made solutions, and in the lower half those of the same solutions, after they had been rotated for the same time and under the same conditions as prevailed in the solubility experiments.

CONDUCTIVITY OF THE POTASSIUM IODIDE AND LEAD NITRATE SOLUTION BEFORE TREATMENT WITH LEAD IODIDE.

	Potassium iodide solution.		Lead nitrate solution.	
Equivalents per liter =	0.003077	0.002000	0.003077	0.002000
First solution	4247	2809	3782	2498
Second solution	4257	2807	3785	2497
Mean	4252	2808	3784	2498
First solution	4288	2836	3771	2487
Second solution	4288	2849	3774	2487
Mean	4288	2843	3773	2487

In order to ascertain the conductivity of the dissolved lead iodide in the presence of the other two salts, we have subtracted the mean values in the lower half of this table from those of the saturated solutions in the two previous tables, it being assumed that the conductivity at these dilutions is an additive property. That this assumption is approximately correct may be concluded

from the fact that the lead nitrate and the potassium iodide at a dilution of 500 liters are 93.6 and 98.5 per cent. respectively dissociated, while at a dilution of 325 liters they are 92.0 and 96.9 per cent. respectively dissociated; in other words, the degree of dissociation is so great, and changes so little with increasing concentration, that it cannot be appreciably affected by the presence of the relatively small amount of lead iodide ions. In order now to derive the corresponding concentrations of the ions from the conductivity values, it is only necessary to divide the latter by the molecular conductivities of the respective salts at infinite dilution. We take as the values of the rates of migration, those calculated by Bredig, namely $K = 70.6$, $I = 72.0$, and $NO_3 = 65.1$ The value for the lead ion has, so far as we know, not as yet been derived. Franke[1] has, to be sure, measured the conductivity of lead nitrate in dilute solution, from which the rate of migration can be calculated. Since, however, this value is for our purpose of fundamental importance, we thought it advisable to confirm the accuracy of his determinations by measurements of our own. We have therefore determined the conductivity of both of our samples of lead nitrate at different dilutions. Our values (represented by μ_1 and μ_2, the mean value by μ), together with those of Franke $(\mu_{Fr})_1$, are given in the following tables.

EQUIVALENT CONDUCTIVITY OF LEAD NITRATE.

V.	μ_1.	μ_2.	μ.	μ_{Fr}.
256	120.8	120.9	120.9	122.2
325	122.6	122.8	122.7	....
500	124.9	124.8	124.9	....
512	125.2	125.3	125.3	125.9
1024	128.2	127.7	128.0	127.1

As is seen, the conductivities of our two samples agree almost completely with each other, and also fairly well with those of Franke. To obtain the value at infinite dilution, we make use of Bredig's[2] extrapolation-values, which have been derived from a consideration of a large number of salts. The values, extrapolated in this manner from our measurements, are, for the three dilutions, 256, 512, and 1024 liters, 132.9, 133.3, and 134.0, re-

[1] *Ztschr. phys. Chem.*, **16**, 471.

[2] *Ibid*, **13**, 198.

spectively. We therefore take the mean, 133.4, as the value of the conductivity of the lead nitrate at infinite dilution.

Since the rate of migration of the NO_3 ions is equal to 65.1, that of the lead ion must be 68.3, from which it follows that lead iodide has for its value at infinite dilution 140.3. Finally, the value derived for potassium iodide at infinite dilution from the above given rates of migration is 142.6. Now, if the corresponding specific conductivities are divided by these limiting values, we obtain the concentrations of the ions which correspond to the conductivity measurements given above. The results of these divisions are presented in the following table, those in the case of the lead iodide being placed under the heading "Found."

CONCENTRATION OF THE IONS IN THE SATURATED SOLUTIONS.

Potassium iodide ions.	Lead iodide ions.		Lead nitrate ions.	Lead iodide ions.	
	Found.	Calculated.		Found.	Calculated.
0.00	0.002873	.....	0.00	0.002873	.....
0.001969	0.001770	0.001731	0.001872	0.002358	0.002369
0.002982	0.001351	0.001296	0.002837	0.002155	0.002175

It is readily seen from these numbers that the solubility in the potassium iodide solutions as well as in those of the lead nitrate, is considerably less than in pure water, and further that the diminution caused by equivalent amounts of the two salts is quite different. We will now compare quantitatively the experimental results with the requirements of the principle of solubility effect.

The laws of mass action require that in the case of a saturated solution of a tri-ionic salt, the product of the concentration of the bivalent ion into the square of the concentration of the univalent ion shall be a constant quantity, whatever other salts may be present at the same time.[1] In this case the equation,

$$Pb \times (I)^2 = \text{a constant},$$

should hold, where the chemical symbols denote the concentrations of the respective ions.

If m_0 is the solubility of lead iodide in pure water, m its solubility in a potassium iodide or lead nitrate solution whose concentration is n (all expressed in equivalents), and a_0, a, and a_1, the corresponding dissociation values, the following equation applies in the case where lead nitrate is present:

[1] *Ztschr. phys. Chem.*, 9, 627.

$$(ma + na_1)\ m^2a^2 = m_0^3a_0^3,$$

and where potassium iodide is present this equation:

$$ma\ (ma + na_1)^2 = m_0^3a_0^3.$$

The value m_0a_0, the concentration of the ions in the saturated solution in pure water, is found to be 0.002873; and the values of na_1, the concentrations of the ions in the lead nitrate and potassium iodide solutions in the four solubility experiments, are given in the first and fourth columns of the last table. From these we have calculated the values of *ma* (the concentration of the lead iodide ions) by the two formulas given above. This cubic equation is easily solved by substituting an estimated value of *ma*, and calculating the value of the left member of the equations, repeating this process until the value thus found becomes equal to $m_0^3a_0^3$. The theoretical values obtained in this way are found in the last table under the headings "calculated."

The agreement between the experimental and the theoretical values, although not complete, is however entirely sufficient to prove the essential correctness of the solubility principle. The deviations are, in the case of the lead nitrate, 0.9 and 0.3 per cent., and in that of the potassium iodide, 4.1 and 2.2 per cent. It is however to be considered that the values of *ma* were not directly measured, but were obtained as the differences of two larger experimentally determined values, whereby the percentage error is greatly increased. In order to give an idea of the existing error relations, it may be mentioned that an error of one-half per cent. in the conductivity of the lead nitrate solution saturated with lead iodide, and an equal error in the subtracted conductivity of the pure lead nitrate solution, would cause in the value *ma* an error which would probably amount to 1.3 per cent. in the 0.003077 normal solution and 0.9 per cent. in the 0.002000 normal solution. Equal errors in the potassium iodide experiments would cause errors of 2.0 and 1.0 per cent. respectively in *ma*. It is therefore seen that the method cannot furnish very accurate results, and that the differences between the actual and the calculated values are not improbably due to experimental errors.

It has therefore been established by this investigation within

the (somewhat wide) limits of experimental errors, that *the solubility of lead iodide is diminished both by potassium iodide and by lead nitrate in such a way that the product of the concentration of the lead ions into the square of the concentration of the iodine ions remains constant.*

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
JANUARY, 1898.

GLUCOSE IN BUTTER.[1]

By C. A. CRAMPTON.

Received January 22, 1898.

I have been unable to find, in the literature of food products or of food adulteration, any reference to the use of glucose or other form of sweetening material in butter. The nearest approach to it is the mention of starch by some of the German authorities as among the possible adulterants. In domestic practice, however, the addition of sugar to butter for purposes of preservation is doubtless almost as old as the art of butter-making itself, sugar and salt being the standard household preservatives for food products from time immemorial. But the use of sugar in this way is comparatively rare, salt being universally preferred as a preservative for this food product as it is for most products of animal origin. Sugar appears in several of the various U. S. Patents for so-called "improving" or renovating processes for butter, being added to it along with salt, saltpeter, and, in some cases, sodium carbonate. The sugar is usually in small quantity in these formulas, perhaps an ounce to eight pounds.

Within the past few years glucose has been used in butter specially prepared for export to tropical countries, as the West Indies or South America. The hot climate of these countries renders its preservation very difficult. It is usually put up in tins and various means are resorted to by the dealers in different nations who export to them for preventing the decomposition of their goods before they reach the consumer. Very large quantities of salt are used by the French exporters. I give below the figures obtained from the analysis of two samples of French butter, as exported, the one to Brazil, the other to the Antilles:

[1] Read at the Washington meeting, December 30, 1897.

	No. 2436. Butter "a la Morlaix" as exported to Brazil.	No. 2437. Butter "a la Morlaix" exported to the Antilles.
Water	10.29	10.19
Curd	1.24	1.31
Ash	10.29	10.06
Fat	78.18	78.44
	100.00	100.00
Figures for Fat.		
Specific gravity at 40° C	9107	9112
Koettstorfer value	227.2	227.3
Reichert-Meissl figure	28.4	29.4

Chemical antiseptics, borax, salicylic acid, etc., are sometimes used, but the method found most efficacious by exporters in this country, so I am informed, is to use glucose in conjunction with a moderately heavy salting. I give below the figures obtained from two samples prepared in this way and exported to Brazil. One of these, No. 2443, has traveled twice across the equator and remained in my refrigerator since its return last August. While it is not exactly attractive to taste or smell, it is still possible to remain on speaking terms with it, which seems to be pretty good evidence of the effect of the glucose upon its keeping qualities.

I have inserted here also the analysis of a sample of so-called *beurre rouge*, or red butter, as exported to Guadeloupe. This is a very peculiar compound, highly colored, and contains large quantities of salt and glucose.

	No. 2434. Butter exported from the United States to Brazil.	No. 2443. Butter exported to Brazil and returned to the U. S.	No. 2460. *Buerre rouge* exported to Guadeloupe.
Water	16.29	18.93	21.60
Curd (N × 6.25)	1.19	1.06	0.81
Ash	7.00	6.19	16.42
Fat	72.16	69.67	51.15
Glucose (by difference)	3.36	4.15	10.02
	100.00	100.00	100.00
Figures for Fat.			
Specific gravity at 40° C.	9093	9090	9080
Koettstorfer value	225.4	225.5	228.1
Reichert-Meissl figure	27.2	25.4	26.4

Through the kindness of a firm of butter exporters I obtained

a sample of butter as purchased by them in western markets, and a sample of the same butter prepared for export by admixture of glucose, salt, and coloring-matter.

Following are the results obtained from these samples:

	No. 2445. Butter purchased in western markets.	No. 2446. Same prepared for export by admixture with glucose and salt.
Water	10.97	17.03
Curd (nitrogen × 6.25)	1.31	0.94
Ash	2.56	8.49
Fat	85.08	70.59
Glucose (by difference)	0.00	2.95
	99.92	100.00
Figures for Fat.		
Specific gravity at 40° C	9114	9110
Koettstorfer value	228.4	227.9
Reichert-Meissl figure	29.6	29.4

I also obtained a sample of the glucose used. It is the heavy, low converted sirup known as confectioners' glucose. It contained 16.5 per cent. of water, and gave $[\alpha]_D = 119.3$; $R = 43.10$.

The detection of glucose in butter presents no difficulty. In making the analysis of a butter containing it by the ordinary method of extracting the fat with ether, weighing the residue, incinerating and determining the curd by the loss on ignition, the presence of the glucose would be manifest by an abnormally high curd, as both would be burned off together. This is shown by the figures obtained in this way for curd in the four samples given above, as compared with the results obtained from the nitrogen determination. In the case of 2445, containing no glucose, the results by the two methods closely agree.

Number.	Percentage of curd obtained by usual method.	Percentage of curd obtained by (N × 6.25).
2434	4.55	1.19
2443	5.21	1.06
2445	1.39	1.31
2446	3.89	0.94
2460	10.83	0.81

In making a direct demonstration of the presence of glucose, I have used the method of washing it out with hot water, in the

manner first recommended by Wiley for the direct estimation of salt in butter and now used by the Association of Official Agricultural Chemists as an official method. Ten grams of the butter are weighed out in a beaker, transferred with hot water to a separatory funnel, where it is treated with successive portions (twenty to thirty cc.) of hot water, and the resulting solution made up, when cooled, to 250 cc.

A slight reduction of copper by this solution must not be taken as a qualitative proof of the presence of glucose in the butter, being due to the small amount of milk sugar present or perhaps to a reducing action by some of the albuminoids. Any considerable precipitation of Fehling's solution, however, may safely be ascribed to the presence of glucose or sugar, and the copper oxide reducing strength of the solution can be readily ascertained. The optical rotation may also be determined, the solution being readily clarified by means of alumina cream or by acid mercuric nitrate solution. The determination of salt can, of course, be made in the same solution, if desired.

In the previous analyses I have given the percentages of glucose as calculated by subtracting the sum of the water, ash, and fat from 100. The figures obtained in this way are not very exact, as the ether removes some of the glucose with the fat, making the figure for the latter too high, and for the former too low. I give below the percentage of glucose in each sample on the assumption that the same kind of glucose was used in Nos. 2434, 2443, and 2460, that I know to have been used in No. 2446, and calculating the figures from both the reducing and rotatory power.

Number.	Percentage of glucose calculated on basis of reducing power.	Percentage of glucose calculated on basis of rotatory power.
2434	5.57	5.64
2443	6.50	6.45
2446	5.10	5.24
2460	13.58	13.30

The relative quantities of butter, salt, and glucose used in No. 2446 were given to me by the manufacturer, as follows: 712 pounds of butter, 50 pounds of salt and 55 pounds of glucose. This would make the content of glucose 6.70 per cent. but it is apparent that considerable water was added as well.

Evidently the direct figures obtained above are much nearer the truth than the results obtained by difference. If the composition of the glucose is not known it could probably be worked out by the formula of Brown, Morris, and Millar.[1]

Butter No. 2443 was condemned by the customs authorities in Brazil, not on account of the presence of glucose, which seems to have escaped the notice of the analyst entirely, but on account of the low figures obtained from the fat, upon which was based a decision that it contained oleomargarine. The Reichert figure is low, but not sufficiently so, in my opinion, to justify the assertion that it was not butter fat. It is not to be presumed that the addition of the glucose would have any influence upon the fat, and the figures obtained in the case of Nos. 2445 and 2446 seem to prove conclusively that it does not.

I have had but few opportunities to examine domestic butters for the presence of glucose and have not found it as yet in any of the samples at hand. Its presence would be most likely, of course, in butters which had been subjected to reworking or renovation. In addition to its preservative action, the glucose probably acts mechanically to hold the large water content of the butter, enabling it to retain more than it otherwise would.

I will not attempt to discuss here the question as to whether or not the addition of glucose to butter constitutes an adulteration. It might be said to admit of some argument, however, as there does not seem to be any good reason, except custom, for preferring salt to sugar as a preservative for butter. Such butter could hardly be considered as coming within the scope of the national law known as the "Oleomargarine Law" as it would in no sense answer the definition of oleomargarine in that law.

DISCUSSION: *G. E. Patrick.*—I should like to know how the author accounts for the very great difference between the figures obtained in the glucose by incineration and that obtained by the direct method.

C. A. Crampton.—By the faulty method of fat determination, I have no doubt the ether takes out some glucose.

G. E. Patrick.—Would not petroleum ether be a better solvent?

[1] *Chem. News.*, 75, 42.

C. A. Crampton.—The suggestion seems to be a good one. I have no doubt it would dissolve less glucose.

In reply to Mr. Elworthy, who stated that butter was now preserved in India on a large scale by the addition of salt only, in hermetically sealed cans, and kept for six or seven months, and who asked whether the figures given were for dry glucose, Mr. Crampton said that the glucose was calculated on the supposition that the same kind of glucose, "confectioners' sirup," had been used in all cases.

A METHOD FOR DETERMINING THE RESISTANCE OF ELECTROLYTES.

By PARKER C. MCILHINEY.

Received January 10, 1898.

THE method commonly used for determining the resistance of an electrolyte is that of Kohlrausch, in which the resistance to be measured is made one arm of a Wheatstone bridge, while the current is an alternating one supplied by an induction coil and the balance is determined by a sensitive telephone instead of the galvanometer used in ordinary measurements. It is a zero method capable of a high degree of accuracy, but it is not very rapid and readings can not be taken at short intervals of time.

The method to be described does not lay claim to so high a degree of accuracy, as it is limited by errors in a galvanometer and by changes in the electromotive force of a battery during an experiment, but it is believed to have some advantages in the possibility of making many readings in a short space of time.

It consists briefly in determining by a galvanometer, preferably a d'Arsonval, the potential difference between the ends of a known resistance placed in series with the resistance to be determined. The current is supplied by a gravity battery and before passing through the electrolyte it is transformed into an alternating current by means of a rotary pole changer, but the current passing through the known resistance is direct.

When a current passes through two resistances in series the fall of potential in each of them is proportional to its resistance.

In Fig. 1, let R be a known resistance, R′ be another known resistance, which may be replaced by the unknown resistance X.

Let f be the fall of potential in R, when R′ is in series with it.
Let g be the fall of potential in R, when X is in series with it.
Let E be a constant electromotive force.

Then

$$f = \frac{RE}{R + R'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

and

$$g = \frac{RE}{R + X} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

from which we get

$$X = \frac{(f-g)\,R + fR'}{g} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

If we determine the fall of potential in R, when R′, the other known resistance is in the series, then replace R′ by X, the unknown resistance, and again determine the fall of potential, we shall be able, by substituting in (3), to determine the value of X. If R be supposed equal to o equation (3) becomes

$$\frac{fR'}{g} = X \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

or

$$g : f :: X : R' \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

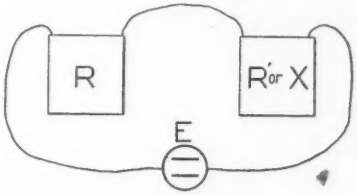

Fig. 1.

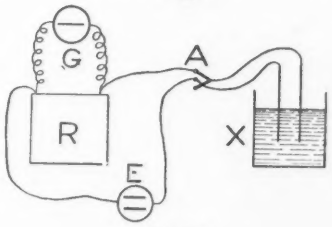

Fig. 2.

If R is very small in comparison with R′, equation (5) may be assumed to be applicable without the introduction of serious

error and the fall of potential in R would then always be proportional to the conductivity of R'.

If the measurement of the fall of potential in R is made by a d'Arsonval galvanometer, which gives readings proportional to the electromotive force of the current passing through it, and R is made small in proportion to R', the readings of the galvanometer give directly the conductivity of the electrolyte.

The method was devised to determine the resistance of silicates and similar substances under the influence of heat and for this purpose many readings had to be made. It proved well adapted to the purpose and probably would be convenient for other experiments in which a great many readings are desired from the same sample.

The apparatus necessary, aside from the containing vessel for the electrolyte and connecting wires, consists of two resistance boxes, one having small resistances, the other preferably containing resistances, of the same order of magnitude as the quantities to be determined, a d'Arsonval galvanometer and a rotary pole changer to convert the direct current from the battery into an alternating one, so as to prevent polarization. The pole changer is a simple machine driven very well by any small motor which gives a fairly regular rotation. The method of connecting the apparatus is shown in Fig. 2.

R is the small resistance box.
X is the electrolyte.
E is a gravity battery.
A is the rotary pole changer.
G is the galvanometer.

The deflection of the galvanometer may be brought to a convenient figure for accurate reading, no matter what value X may have, by altering the value of R. The resistance of the galvanometer must be known, in order to make the calculation. Part of the current coming to the terminals of R passes through the galvanometer, and hence the resistance of the two together is slightly less than that of R alone. If we call the resistance of the galvanometer S, then the resistance of R and S together $= \frac{R\,S}{R+S}$. Here if R is small enough in proportion to S the con-

ductivity of the galvanometer may be neglected, and if R is changed to obtain a deflection more suitable for reading, the two readings may, without sensible error, be assumed proportional to the two values of R.

Changing R of course changes the sensitiveness of the whole arrangement and this may be done to as great an extent as the coils in R will allow. If it contains coils of one-tenth to twenty ohms the sensitiveness may be varied two hundredfold by a change in plugs, an operation requiring only a few seconds. In the work on heated silicates the resistance varied with the temperature from a comparatively small figure to practical infinity and the method made its determination quite simple, particularly as the same galvanometer was used for determining conductivity and for determining temperature by the thermoelectric method. Alternate readings of temperature and conductivity were taken at intervals of some seconds during the cooling of the materials from a high temperature by the use of a suitably disposed double switch.

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THE COMMERCIAL ANALYSIS OF BAUXITE.

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THE bauxite mined in Georgia and Alabama, constituting practically all of the domestic supply, is used for the manufacture of alum and aluminum, in the proportion of about three-fourths to one-fourth. The analytical methods hitherto employed have been based, to a considerable extent, upon the purposes to which the material was applied.

It is obvious that the easy solubility of the alumina in sulphuric acid is a great desideratum for the manufacturer of alum, and furthermore, that the acidulated mass should filter readily, and be capable of rapid washing.

But it is generally impracticable for the ordinary chemist to base his methods on factory tests, for the reason that these are, for the most part, unknown to him. All that can reasonably be required of him is that his methods should not yield results widely at variance with those obtained on a large scale in actual operations.

Were the question of bauxite analysis one solely of the total amount of alumina, almost any of the methods used for the estimation of this substance in the presence of silica, oxide of iron, and titanic acid could be employed. But the total amount of alumina is of secondary importance as compared with its ready solubility in sulphuric acid, in the manufacture of alum.

Whatever may be said as to the requirements of the manufacturers of aluminum, it is certainly necessary in the manufacture of alum that sulphuric acid should readily dissolve the alumina. One might go a step further and allow that the residue after treating with acid should be of such nature as to permit of rapid and thorough washing. This latter consideration, however, is not of such vital importance in the valuation of bauxite as that the material should dissolve readily in the acid, and that no substance deleterious in alum-making should at the same time go into solution. It seems to us that there are four main points to be considered in valuing bauxite by analysis for alum-making. Ranging them in the order of their relative importance they are as follows :

1. Easy solubility of the alumina in sulphuric acid.
2. Rapid filtration.
3. Rapid washing.
4. Freedom from substances that on going into solution would affect the quality of the alum, or other products.

There may be, of course, a difference of opinion as to the relative importance of the second, third, and fourth considerations but there can be no doubt of the rank of the first.

If the bauxite is ferruginous, the fourth point may come second, but at present and for some time to come the purer bauxite alone will come into the market. There is very little demand for second grade material, and while the percentage of ferric oxide is to be held in view in valuing even the pure bauxite it is not of much importance for the reason that it is generally very small.

The Georgia-Alabama bauxite consists of the trihydrate of alumina, $Al_2(OH)_6$, or $Al_2O_3.3H_2O$, mixed with clay, and what may prove to be a lower hydrate of alumina, possibly $Al_2O_3.2H_2O$.

There are three well recognized hydrates of alumina—the monohydrate (diaspore), $Al_2O_3.H_2O$ or $Al_2O_3(OH)_2$, containing

	Per cent.
Alumina	85.02
Water	14.98

the dihydrate, $Al_2O_3.2H_2O$ or $Al_2O(OH)_4$, with

	Per cent.
Alumina	73.94
Water	26.06

and the trihydrate (Hydrargillite, Gibbsite), with

	Per cent.
Alumina	65.41
Water	34.59

The formula for bauxite, $(AlFe)_2O(OH)_4$, given by Roscoe and Schorlemmer[1] does not seem to apply to the American material. Assuming for the present that the domestic bauxite is a mixture of alumina trihydrate, clay, and possibly a lower hydrate, the methods adopted for its analysis, so far as concerns the alum-maker, should be based upon the estimation of two different things: (1) the amount of alumina existing as trihydrate, and very readily soluble in sulphuric acid, and (2) that existing as some other compound, whether a lower hydrate, or clay, less soluble in the acid, but which in the process of manufacture can be utilized. It would appear that the more easily soluble alumina should have a higher value placed upon it than the other. It costs less to make alum of material easily soluble than of material difficultly soluble, and if there exists in bauxite two or more alumina compounds, differing markedly from each other in solubility, the consumer is entitled to know what are the proportions between them.

Heretofore the analytical methods adopted, outside of factories, for the valuation of bauxite, have resulted in giving practically all of the alumina, and no efforts have been made, so far as known to us, to discriminate between the alumina compounds present.

The two methods ordinarily used are the Pittsburg, worked out by Mr. Jas. O. Handy, and the Spence method. Both of these agree in evaporating the mixture of sulphuric acid and bauxite to fumes of the so-called sulphuric anhydride and continuing the heat for some minutes. Mr. Handy recommends a mixture of

[1] Treatise on Chemistry, 2, [1], 444.

hydrochloric acid of 1.20 sp. gr., nitric acid of 1.42 sp. gr., and sulphuric acid of 1.20 sp. gr., in the respective ratio of 1 : 3 : 6. Mr. Spence uses a mixture of equal parts of strong sulphuric acid and water. In each case the ratio between acid mixture and bauxite is the same ; *viz.*, one gram bauxite and 5 cc. acid. In using either method, taking up the residue in water, boiling, filtering, and washing thoroughly, very little alumina will be found in the residue. From numerous analyses we have found that considerably less than one per cent. of alumina is left in the residue, so that it may be said that practically all of it is dissolved.

More or less objection has been urged by alum-makers, to these methods. They have claimed that for their purposes the yield of alumina is too high, that by carrying the analytical treatment to fumes, whether using the mixture of acids, or sulphuric acid alone, compounds of alumina, which are not suited for the manufacture of alum, are decomposed and dissolved, and consequently the percentage of alumina does not represent what may fairly be considered as soluble alumina.

Aside from manufacturing processes, upon the discussion of which we do not enter, the objections seemed reasonable, and we began a series of investigations on commercial bauxite, not so much with the purpose of studying the exact composition of this material as of ascertaining whether a practical method of discriminating between the several compounds of alumina present in bauxite could be worked out. The results reached are extremely interesting and important alike to the shippers and the consumers, for they seem to indicate that it is perfectly feasible to determine the alumina existing as trihydrate, and therefore readily soluble, and the alumina as clay, or as a lower hydrate, and of less solubility.

From a lot of about 300 pounds of bauxite taken from the loading shed of a company actively engaged in mining and shipping for alum works, five separate samples were taken.

A. A general average of the whole lot, lump and fine.

B. A white, friable material, with no iron stains.

C. A compact, cream-colored variety, with conchoidal fracture and pearly luster.

D. A variety full of nodules considerably stained with iron.

E. A clay, probably halloysite.

A separation of these varieties by elutriation was not possible, as they gave the following specific gravities:

	Sp. gr.
B	1.77
C	1.74
D	1.74
E	1.76

Two grams of A, through a sixty-mesh sieve, were treated with ten cc. sulphuric acid of 50° B., in a steam-bath at 100° C., for the time given below, 100 cc. water added, and the contents of the flask heated in the bath for ten minutes. It was then filtered, and washed thoroughly with hot water.

	Per cent.
Alumina extracted in two hours	53.37
" " " one hour	53.18
" " " one hour	53.21
" " " one-half hour	51.27

The other samples were similarly treated for one hour. None of the solutions contained titanic acid, and only a small percentage of iron oxide was dissolved.

The insoluble residues were dried at 100° on tared filters, and weighed, then ignited and weighed again, the difference being taken as combined water. The amount of water combined with the alumina dissolved was ascertained in two ways:

1. By deducting the weight of the insoluble residue, dried at 100° from the total weight of substance taken, and, from this result, deducting the sum of the weights of alumina, ferric oxide, and moisture.

2. By deducting from the total loss on ignition the amount of combined water in the insoluble residue, and moisture.

The first method is probably more nearly correct.

The results of the analyses are as follows:

SOLUBLE PORTION.

	A.	B.	C.	D.	E.
Moisture	0.70	0.38	0.94	0.56	0.45
Ferric oxide	0.93	0.21	0.21	0.96	0.20
Alumina	53.21	58.03	58.94	48.69	3.11
Combined Water (1st method)	28.28	30.78	31.00	25.77	1.87
" Water (2nd method)	28.17	31.14	31.31	25.90	1.05
" Water (mean of 1st and 2nd)	28.23	30.96	31.15	25.83	1.46
" Water (calculated)	28.20	30.75	31.26	25.80	1.64

INSOLUBLE PORTION.

Combined Water	1.79	1.10	0.91	2.59	12.83
Alumina	4.15	2.69	2.39	7.48	37.70
Silica	7.28	3.06	2.40	8.85	42.88
Titanium oxide	3.63	3.70	3.08	4.82	1.10

These results point strongly to the formula $Al_2O_3.3H_2O$, or $Al_2(OH)_6$, for the substance dissolved. The iron is probably in the hydrated condition. If so, this would introduce a small correction, which however would be partially compensated by slight action on the clay residue, which will be mentioned later on. The figures for the soluble part have been verified in every case by duplicates, and in some cases by many analyses; as for instance in E, where it becomes very difficult to obtain accurately the per cent. of water, owing to the large amount of insoluble residue.

Little can be said as to the composition of the insoluble residue, but these results and many others which do not properly belong to the present discussion, seem to indicate that it consists chiefly of a halloysite or kaolinite clay; and that the larger portion of the titanium exists as the hydrated oxide, either titanic or metatitanic acid; that it also contains variable amounts of quartz or silicious sand; and it is not improbable that corundum and rutile are present in minute amounts, though neither have been identified with certainty.

The valuable constituent beyond a doubt is aluminum trihydrate, and the most reasonable settlement of the commercial question, it seems, would be to make this the basis of sales in the future. It might be argued that the alumina yield would be larger in this case than the analysis would indicate, as ordinary treatment will remove some alumina from clay.

To arrive at a fair conclusion in regard to the matter, it would appear to be necessary to further limit and define the word "bauxite" as applied to the Georgia-Alabama mineral. If the results given in this paper prove anything, they certainly show that in the so-called bauxite there is a sharp line of division as regards chemical action under certain conditions.

In outlining this work originally, it was intended to treat samples at various degrees of temperature, with various strengths of acid, the samples also to vary in their state of subdivision.

Other work has however prevented this, but enough has been done to throw some light on the question here involved. Acid of 40° B. dissolves practically the same per cent. of alumina as acid of 50° B. The substance passed through a sixty-mesh sieve gives the same per cent. of soluble alumina, as when all is passed through a 100-mesh sieve.

Some results have already been given showing difference in time of treatment. All results obtained indicate that if any of these variables of time, temperature, strength of acid, or subdivision be taken in regularly increasing increments, the per cent. of alumina dissolved increases rapidly at first and soon becomes fixed, the ratio $Al_2O_3.3H_2O$ being unaffected, and afterwards the per cent. of alumina increases again, the ratio then approaching $Al_2O_3.H2_2O$.

Clearer proof could hardly be desired that bauxite, as we know it, is a mixture, and not a true chemical compound. The same result exactly would be obtained if workmen were directed to mix clay and the mineral, and the chemical methods now in use would not detect the change, at least only partially. They would show a lowering of the per cent. of alumina and increase of silica, but in nothing like the true amount of the addition, while a determination of $Al_2(OH)_6$ would detect it absolutely.

In order to establish the method on a scientific basis it is required to prove (1) that all alumina existing as $Al_2O_3.3H_2O$ is extracted and (2) that it is contaminated by alumina from no other source.

Samples A and E were used for this purpose, the alumina being first extracted in the usual way using two grams of substance and fifteen cc. of 50° B. sulphuric acid at 100° C. for one hour, the residues washed free of alumina and dried at 100°, retreated in the same way, etc.

	Percentage of soluble alumina. A.	E.
First extraction.....	53.18	3.21
Second "	0.22	1.20
Third "	....	1.08

Certainly no considerable amount of $Al_2O_3.3H_2O$, could have remained or it would have appeared in the second extraction of A, but it seems that the reagent decomposes clay slowly as is shown

by E and it is probable that the additional alumina in A comes from the clay of the residue. It is intended at some time in the future to ascertain the minimum strength of acid which will extract at 100° C. in one hour all $Al_2O_3.3H_2O$, and it is possible that the action on clay may become very slight and a correction be determined and applied.

Results are quite close enough for commercial purposes, and, while it is possible that they may vary three- or four-tenths or even five-tenths of one per cent. from the true figure for alumina existing as $Al_2O_3.3H_2O$, the error is always in the same direction, and when the process is carried out in exactly the same way each time, results are remarkably concordant.

As illustrating this the following results are given ; they were made as checks on per cent. of soluble alumina.

	A.	B.	D.	E.	D.
1	53.21	58.03	58.94	48.69	3.11
2	53.18	58.00	59.05	48.80	3.12
3	53.14	58.10	59.00	....	3.08
4	53.26	....	....	....	....

It should be noticed that the error of the determination will depend upon the amount of the residue. A bauxite of average composition would give about twenty per cent. of insoluble residue, and the soluble alumina would probably be 0.25 per cent. too high, and the calculated $Al_2(OH)_6$ about 0.35 per cent. too high.

We beg, therefore, to recommend that, instead of carrying the analytical treatment to fumes of so-called sulphur trioxide, there be substituted the treatment with 50° B. sulphuric acid at 100° C. for one hour. We give at the conclusion of this paper our method of analysis. It may be of interest here to give some comparative results by the different methods.

A bauxite, containing by the Pittsburg method 59.20 per cent. of soluble alumina, was found by our method to contain 57.22 per cent. Another sample with 56.26 per cent. of soluble alumina by the Pittsburg method gave by our method 53.38 per cent.

A sample with sixty per cent. soluble alumina by the Pittsburg method gave us fifty-nine per cent., another with 54.87 per cent. gave us fifty-three per cent. Speaking generally we have found

that the difference between the Pittsburg method, or the Spence, and our method is less the purer the bauxite. This result may be anticipated, for the purer the bauxite the more of the alumina does it contain as the trihydrate.

Under the proposed change in the method of valuing bauxite it would be necessary to fix upon some name for the alumina dissolved at 100° by sulphuric acid of 50° B., and for that dissolved at fumes. We suggest the term " free alumina" for the alumina dissolved at 100° C. and " combined alumina" for the difference between this and the alumina dissolved at fumes, the sum of the two to be known as " available alumina." For instance, if a bauxite contained fifty-four per cent. of alumina soluble in 50° B. acid in one hour at 100° C. it would contain fifty-four per cent. of free alumina. If by the Pittsburg or the Spence method there was found fifty-eight per cent. " soluble alumina," we would now call this fifty-eight per cent. of " available alumina," and there would be four per cent. of " combined alumina."

There is an objection to this system of nomenclature in that the free alumina is really combined, just as much so as the additional alumina extracted by fuming acid. It being combined with water in the form of the trihydrate, the exact meaning of the term should be that the free alumina is the alumina from the trihydrate, and easily soluble in sulphuric acid. This much may be taken as proved. We can not state, at present, in what form the alumina exists that we propose to call " combined alumina." It may be as clay, as a lower hydrate, or as a form of Al_2O_3 itself, insoluble except in fuming acid. It does not greatly matter in what form it exists, the chief thing to be considered being that it is not soluble in 50° B. sulphuric acid at 100° C., but is soluble in acid brought to fumes.

It is not in the province of this paper to assign exact commercial values to the free and the combined alumina, or to the free and the available alumina, as this should be left to the decision of the miners and the consumers. In the fertilizer trade it has not been found difficult to agree upon the price of water-soluble phosphoric acid, and available phosphoric acid, this latter being the sum of the soluble and the reverted. Acid phosphate

is now offered in bulk at so many cents per unit of available phosphoric acid, and the higher the percentage of the available acid the higher the price per unit.

We propose to introduce into the alum trade a system which has been used for many years in the fertilizer trade, and which has been found to be extremely useful. In bauxite the difference between the easily soluble trihydrate, and the difficultly soluble alumina in the residue, should be considered.

We are convinced that the changes proposed would be for the benefit of all concerned. Take for instance the case of a shipper who is sending out bauxite containing clay, such as E, and we beg to say again that E was taken from a lot of bauxite ready for shipment. If the prepared bauxite should contain an undue proportion of E, with only 3.11 per cent. of free (or easily soluble) alumina, it goes without saying that its value for alum-making would be seriously impaired. Comparing E with C (and both varieties came from the same bag) E has 3.11 per cent. of free alumina, and C has 58.94 per cent; in the insoluble portion E had 37.70 per cent. of alumina, and C had 2.39 per cent. In other words the free alumina in E was 7.62 per cent. of the total alumina, and in C it was 96.10 per cent.

Take another instance. With the very best bauxite there occurs a white clay which, when the material is ready for shipment, can not be distinguished from the bauxite itself. It may be mixed with the bauxite in considerable proportions and yet fail of recognition, because its physical qualities so nearly approximate those of pure bauxite. In the pits the lines of separation between bauxite and clay are perceptible indeed to the trained eye, but it is practically impossible to prevent the miners from overrunning the line. This is both theoretically and practically true. The situation at the mines renders it theoretically impossible to keep the clay out of the bauxite, and samples of clay picked out of the bauxite already mined show that it does occur in it. In pure bauxite the proportion of clay is at the minimum when the mine is operated from the middle of a big pocket of bauxite, but as the mining nears the sides of the pocket and approaches a bed of clay, the danger of admixture of clay increases, and when the pocket is almost exhausted and the mining is carried on close to the clay, more or less of this sub-

stance is sure to get in. The quality of the Georgia-Alabama bauxite is sufficiently high, as proved by the low silica and high free alumina, to preclude the possibility of there being much clay in it, but some clay is always present so far as our observation goes, covering several years.

We have ourselves obtained samples of these clays from the bauxite mines. One of them came from immediately next to a pure bauxite. It contained 41.80 per cent. of total alumina, of which 2.08 per cent. was free, 37.75 per cent. combined, and 1.97 per cent. insoluble. Of the total alumina 4.97 per cent. was free and easily soluble, 90.31 per cent. was 'combined' and difficultly soluble, and 4.72 per cent. was insoluble in fuming acid.

Another sample gave 43.00 per cent. of total alumina, of which 3.00 per cent. was 'free,' 37.40 per cent. 'combined,' and 2.60 per cent. insoluble. Of the total alumina 6.97 per cent. was 'free,' 86.98 per cent. was 'combined,' and 6.05 per cent. was insoluble.

Compare these results with those obtained from sample E, remembering that these two were clay taken from the mines, and E is clay taken from bauxite already mined. For convenience of reference we will call the two clays F and G, and put the comparative results in a table.

TABLE I.—CLAYS.

Sample.	Free alumina.	Combined alumina.	Available alumina.	Insoluble alumina.	Total alumina.	Total alumina = 100.			
						Free.	Combined	Available.	Insoluble.
E.	3.11	35.45	38.56	2.25	40.81	7.62	86.86	94.48	5.52
F.	2.08	37.75	39.83	1.97	41.80	4.97	90.31	95.28	4.72
G.	3.00	37.40	40.40	2.60	43.00	6.97	86.98	93.95	6.05

Now take three good bauxites:

TABLE II.—BAUXITES.

A	53.21	3.55	56.76	0.60	57.36	92.76	6.19	98.95	1.05
B.	58.03	2.29	60.32	0.40	60.72	95.57	3.77	99.34	0.66
C.	58.94	2.04	60.98	0.35	61.33	96.10	3.32	99.42	0.58

The analyses show very clearly that treatment with sulphuric acid to fumes dissolves alumina from such clays as occur with

and in bauxite, and that treatment with acid at 100° C. does not dissolve this alumina. As regards bauxite itself the treatment at 100° C. serves to discriminate between the alumina of the trihydrate and the alumina of clay, or of a lower hydration.

As to calcining the bauxite before shipment in order to remove the water of hydration, we do not think it advisable. In well arranged bauxite plants the material is now heated in revolving cylinders to remove hygroscopic water, but the temperature should not be great enough to cause loss of combined water. In order to test the effect of loss of combined water on the solubility of the alumina at 100° C. we selected a very pure variety of bauxite, and deprived it, by careful heating, of various percentages of its combined water, and then extracted the alumina with 50° B. sulphuric acid at 100°.

The results are in Table III.

The sample contained 60 per cent. of alumina.

EFFECT OF CALCINING ON SOLUBILITY.

TABLE III.

	Soluble alumina. Per cent.
Dried at 100° C. not calcined	59.00
Loss on calcining, 12.55 per cent	57.60
" " 18.55 " "	57.10
" " 26.60 " "	53.10
" " 32.15 " "	20.40

Calcination certainly tends to decrease the solubility of the alumina, but does not constitute a serious menace until about 80 per cent. of the total combined water is removed. With a loss of about 38 per cent. of the water there is a loss of 1.40 per cent. soluble alumina; with a loss of about 58 per cent. of the combined water the loss of soluble alumina is 1.9 per cent.; with a loss of about 82 per cent. of the combined water there is a much greater loss of soluble alumina; *viz.*, 5.9 per cent. while the loss of soluble alumina rises to 38.60 per cent., when the material is thoroughly calcined. These results would seem to indicate that the material could be calcined until something more than half of its combined water was removed, without seriously affecting the solubility of the alumina, but the practical difficulties in the way of maintaining a uniform calcination at this point would certainly have to be considered. Unless the saving in freight would

more than counterbalance the loss in soluble alumina, there would appear to be no good reason for calcining. The percentage of available alumina (*i. e.*, the alumina dissolved by carrying the treatment with acid to fumes of so-called sulphur trioxide) is decreased by thoroughly calcining the bauxite, but the loss is not serious. In one experiment the 'available' alumina in the sample, dried at 100° C., was 57.20 per cent. and in the thoroughly calcined material 56.40 per cent.; in another sample 55.30 per cent. and 54.54 per cent. In one sample the loss was more considerable, the percentages being 54.87 per cent. and 49.50 per cent.

On the whole we can not recommend that the analytical sample be calcined previous to treatment with acid, whether by the old or the proposed new method, as a serious loss of dissolved alumina *may* be the result.

ANALYTICAL METHOD RECOMMENDED.

The analytical sample is to be passed through a sieve of 100 meshes per linear inch.

Moisture.—Two grams to constant weight at 100° C.

Available Alumina.—Two grams bauxite, ten cc. cold sulphuric acid of 50° B.

Heat gradually in a casserole until fumes of the so-called sulphuric anhydride appear, stirring the while to break up any small pieces; cover with a watch-glass and heat for ten minutes. Cool, add 100 cc. hot water, and boil for five minutes. Filter, and wash free of acid and alum with hot water. Cool filtrate, make up to 200 cc., and take out fifty cc. (equal to five-tenths gram) for alumina, ferric oxide, and titanium dioxide, and fifty cc. for titanium dioxide and ferric oxide, TiO_2 and Fe_2O_3.

Estimation of Available Alumina.—The fifty cc. (equal to five-tenths gram) is diluted to 300 cc., two cc. hydrochloric acid added, heated to boiling, and ammonia added slowly to slight excess. The contents of the beaker are kept boiling for five minutes, filtered hot, and thoroughly washed with hot water. The precipitate is dried, ignited, and weighed as Al_2O_3, Fe_2O_3, TiO_2. The Al_2O_3 is given by subtracting the Fe_2O_3 and TiO_2, obtained in other operations.

Estimation of Titanium Dioxide.—Fifty cc. (equal to five-tenths gram) of the main solution are carefully neutralized with ammonia, the ammonia being added until there is a slight permanent precipitate. This precipitate is dissolved in sulphuric acid, added carefully so that there shall be but a slight excess; the volume is then made up to 350 to 400 cc. and boiled for one hour. If much iron is present, shown by the color of the main solution, it is best to deoxidize with sulphur dioxide, led into the boiling solution in which the titanium dioxide is being precipitated, but if there is only a small amount of iron present sulphurous acid may be used. In either case, however, it is well to maintain the volume of the boiling solution at about the same point, by addition of fresh portions of water, and to be sure that it smells of sulphur dioxide during the boiling. By observing these precautions the titanium dioxide is completely precipitated practically free of iron. Filter hot, through double filters, and wash thoroughly with hot water, dry, ignite, and weigh as titanium dioxide.

Estimation of Ferric Oxide.—This is best determined in the filtrate from titanium dioxide, by reduction with zinc and titration with permanganate.

The weight of $TiO_2 + Fe_2O_3$ subtracted from the weight of $Fe_2O_3 + Al_2O_3 + TiO_2$ gives the Al_2O_3, and this is the "available alumina."

Estimation of "Free Alumina."—Two grams bauxite, ten cc. 50° B. sulphuric acid, in a four-ounce Erlenmeyer flask, provided with a perforated stopper. Heat for one hour in a water-bath at a temperature of 95° to 100° C. with frequent shaking. Add 100 cc. hot water and keep in bath for ten minutes. Filter, wash thoroughly with hot water, and for the estimation of alumina proceed as before, with this difference, however, that the titanium dioxide does not have to be determined, since none of it goes into solution. In the solution we have merely the free alumina, and a small amount of ferric oxide, which can be estimated in the usual manner and its weight subtracted from the weight of the $Al_2O_3 + Fe_2O_3$.

Combined Alumina.—The difference between the available alumina and the free alumina is the combined alumina.

We do not at this time wish to give an opinion as to the form in which this alumina exists. It may be as clay, as a lower hydrate, or a mixture of these and other alumina compounds. We have thus far disregarded the insoluble residue, whether from the acid carried to fumes, or from the treatment at 100° C.

In case it is desired to determine the total alumina, the total titanic acid, the total ferric oxide, and the silica, the insoluble residue from the treatment to fumes may be folded up in the paper, and ignited. When the paper is consumed, fuse the residue with potassium bisulphate, and allow to stand in cold water containing at least five per cent. of strong sulphuric acid several hours, or until completely decomposed. Filter off the silica, which should be perfectly white, wash thoroughly with cold water, and ignite the silica. In the filtrate the alumina, titanium dioxide and ferric oxide are determined as in the filtrate containing the available alumina. Adding these several amounts to those found in the estimation of the available alumina gives, of course, the totals.

We can not advise the determination of silica in the insoluble residue by treatment with hydrofluoric acid and sulphuric acid, as we have found that some of the titanium dioxide is also volatilized, and the loss is $SiO_2 + TiO_2$.

So far as we are aware Riley was the first to point out the volatilization of titanium dioxide as fluoride. It may be that some if not all of what is volatilized goes off as hydrogen titanofluoride, as Roscoe and Schorlemmer[1] state, that when titanium dioxide is dissolved in hydrofluoric acid, a sirupy liquid is obtained which is probably hydrogen titanofluoride, H_2TiF_6. Crookes,[2] in speaking of the estimation of titanium dioxide in silicious residues, says that on treating them with hydrofluoric acid "a titanium fluoride is formed at the same time, which can not be heated without the larger portion going off." He quotes an experiment of Riley's in which 2.235 grams of titanium dioxide were dissolved in hydrofluoric acid, evaporated and ignited, and the residue weighed only 0.99 gram, a loss of 1.245 grams or 55.70 per cent. of the original weight.

By seven successive treatments of titanium dioxide with

[1] Treatise on Chemistry, **2**, [II], 262.

[2] Select Methods in Chemical Analysis, Second Edition, p. 193.

hydrofluoric acid we found the following losses on 0.0700 gram; *viz.*:

	Per cent.
0.0025	3.57
0.0240	34.28
0.0135	19.29
0.0058	8.29
0.0032	4.57
0.0015	2.14
0.0001	0.14
0.0506	72.28

While there is a gain in time by treating the insoluble residue with hydrofluoric acid and sulphuric acid and taking the loss as silica, and while the error introduced is, perhaps, of no consequence commercially, yet the fusion with potassium bisulphate is to be preferred. But unless the silica, and the total alumina, titanium dioxide and iron are required, it is not necessary to make a fusion, the data obtained by the two separate treatments with acid being, in most cases, entirely sufficient for the valuation of bauxite.

So far as our observation goes, and we analyzed many different kinds of bauxite, titanium dioxide is always present, and in some bauxites may rise to four per cent. The clay immediately next to the bauxite may contain one per cent. of titanium dioxide, as we have found eight-tenths per cent. In other clays associated with bauxite we have found mere traces, and in the nearby soils it rarely exceeds five-tenths per cent. The concentration of the titanium dioxide in the bauxite is a very interesting phenomenon, and worthy of more extended investigation.

The titanium dioxide in bauxite is partly soluble in sulphuric acid brought to fumes. By using the Pittsburg method in bauxite acid analysis, or sulphuric acid alone to fumes, varying amounts of titanium dioxide are dissolved, as the following results show:

Total titanium dioxide.	Soluble titanium dioxide.	Per cent. soluble.
4.00	3.30	82.50
3.00	2.60	93.33
4.00	2.50	62.50

The percentage of soluble titanium dioxide, calculated on the total amount present, may fall as low as fifty per cent., but for the

most part appears to be about seventy-five per cent. No titanium dioxide seems to be dissolved by the acid at 100° C. during one hour, but as the temperature rises the solubility increases, and when brought to fumes considerably more than half is dissolved. The variations in the amount dissolved may be due to variations of the form in which the titanium dioxide is present, but on this point we have no definite information. In summing up the chief points in this paper, we desire to call attention to the following:

1. The importance of discriminating in the analysis of bauxite between the trihydrate of alumina, easily soluble in sulphuric acid, and the other compounds of alumina, difficultly soluble.

2. A change in the basis of valuation, by which the trihydrate of alumina is to be given a higher value than the alumina present in some other form.

3. The adoption of a new nomenclature, calling the alumina soluble in 50° B. sulphuric acid at 100° C. during one hour "free alumina," and that soluble in sulphuric acid to fumes "available alumina," the difference between them to be known as "combined alumina."

4. The adoption of a standard method of analysis binding alike on the producer, the broker, and the consumer of bauxite for alum-making.

THE PHILLIPS TESTING LABORATORY,
BIRMINGHAM, ALA.

UPON THE SALTS OF HYDRONITRIC ACID.

By L. M. DENNIS AND C. H. BENEDICT, with Crystallographic Notes by A. C. GILL.

Received January 20, 1898.

IN the year 1890 Th. Curtius announced[1] his successful preparation of hydronitric acid (HN_3), and briefly described the trinitrides of barium (BaN_6), silver (AgN_3), and mercury (Hg_2N_6). He mentioned also the existence of trinitrides of copper, iron, sodium, and ammonium. Since that time no further work upon the inorganic compounds of this most interesting acid was published until last year when thallous trinitride (TlN_3) and thallous thallic trinitride ($TlN_3.TlN_9$) were added to the list.[2] Having a large amount of the acid on hand, we have entered upon the systematic study of the compounds of hydroni-

[1] *Ber. d. chem. Ges.*, **23**, 3023.

[2] Dennis and Doan: this Journal, **18**, 970.

tric acid, and in this paper are given the results obtained with the elements in the principal group of Group I and the alkaline earths of Group II.

GROUP I.

Lithium Trinitride, $LiN_3.H_2O$.—This was made by neutralizing lithium hydroxide with hydronitric acid and allowing the solution to evaporate in the air. It separated in the form of colorless, glistening needles. It is very soluble in water and is hygroscopic. It is also soluble in alcohol. On being gently heated, the crystals lose their luster and water of crystallization is driven off. On further heating the salt breaks down, the decomposition being somewhat more violent than with the other compounds in this group. Upon standing, the lithium trinitride loses some hydronitric acid.

The hydronitric acid was determined by dissolving the salt in water, precipitating with silver nitrate, and converting the silver trinitride into silver chloride.[1] To the filtrate and washings from the first precipitation hydrochloric acid was added to precipitate the excess of silver, the silver chloride was filtered off, and the filtrate and washings were evaporated to dryness with sulphuric acid. The lithium was then weighed as the anhydrous sulphate. Analysis gave as follows:

	Calculated for $LiN_3.H_2O$.	Found.
Lithium	62.72	63.03
Nitrogen	10.46	10.17
Water	26.82	(Diff.) 26.90

Sodium Trinitride, NaN_3.—This salt is mentioned by Curtius but he gives no analysis. It was prepared by the same method as that used for lithium, and upon evaporation of the solution it separates in clear colorless crystals. A freshly prepared aqueous solution of the crystals is neutral in reaction, but, upon standing, it becomes alkaline. The salt does not decompose easily when heated, but on the contrary may be melted and kept in a state of fusion for some hours without breaking down.

The analysis, which was made as described under lithium, gave as follows:

[1] Dennis: This Journal, **18**, 950.

	Calculated for NaN_3.	Found.
Sodium	35.38	35.42
Nitrogen	64.62	64.71

Potassium Trinitride, KN_3.—This compound, like all of the other trinitrides in this group, was made by neutralizing the hydroxide with hydronitric acid. On attempting to concentrate this solution on the water-bath, it became strongly alkaline. This loss of hydronitric acid was determined in one case by neutralizing a solution of potassium hydroxide with a known amount of the acid, evaporating to dryness on the water-bath and determining the acid in the residue. It was found that about four per cent. of the acid had passed off during the evaporation. To obtain crystals of the potassium salt the solution was allowed to evaporate spontaneously in the air and was kept very slightly acid by adding a drop or two of hydronitric acid every day. The salt crystallizes well and the crystals are stable in the air. They melt when heated and decompose only at a high temperature. Potassium trinitride is but slightly soluble in alcohol and is precipitated from aqueous solution by the addition of an excess of alcohol. Analysis gave

	Calculated for KN_3.	Found.
Potassium	48.21	47.92
Nitrogen	51.79	51.72

Rubidium Trinitride, RbN_3.—This salt crystallizes in the form of fine needles. It is extremely soluble in water but is less soluble in alcohol than the potassium salt and, like it, can be thrown out of solution by the addition of alcohol. It fuses when gently heated and at a high temperature it decomposes with a puff and a flash. Analysis gave

	Calculated for RbN_3.	Found.
Rubidium	32.99	32.58
Nitrogen	67.01	67.01

Cesium Trinitride, CsN_3.—On evaporating the solution of this salt it was found to lose hydronitric acid in spite of the strongly basic nature of the cesium. The trinitride was so very soluble in water that crystallization was brought about only by placing it over sulphuric acid. The crystals appeared as clear, colorless

needles, gathered together in fern-like clusters. The salt is almost completely insoluble in alcohol. The crystals decompose only when highly heated. Analysis gave

	Calculated for CsN_3.	Found.
Cesium	75.99	76.03
Nitrogen	24.01	24.36

All of these trinitrides of the alkalies are quite stable in the air, the lithium salt being the only one that tends to lose a part of its acid on exposure. None of the salts are what we should term explosive and the ease of decomposition by heat decreases as the atomic mass of the base rises. In solubility they resemble the chlorides of the alkalies, all of them being soluble in water and the solubility increasing with the atomic mass of the base. The solubility in alcohol is the reverse of that in water, lithium trinitride being quite soluble in alcohol and cesium trinitride being insoluble.

THE ALKALINE EARTHS.

Calcium Trinitride, CaN_6.—This was prepared by dissolving calcium oxide in a dilute solution of the acid and crystallizing over sulphuric acid, the solution decomposing if evaporated on the water-bath. The crystals separate as small, white hemispherical aggregations which under the microscope are seen to be made up of very small crystals of unrecognizable form. The salt explodes with considerable violence when heated. In analyzing the trinitrides of the alkaline earths, the hydronitric acid was determined in one portion by the method above described, and another portion was treated with sulphuric acid and the base weighed as the sulphate. The results for the calcium salt were

	Calculated for CaN_6.	Found.
Calcium	67.74	67.63
Nitrogen	32.26	31.97

Strontium Trinitride, SrN_6.—This was prepared by dissolving strontium oxide in a two per cent. solution of hydronitric acid, and crystallizing over sulphuric acid. The crystals separate in the same peculiar hemispherical form as does the calcium trinitride. The strontium trinitride is more soluble in water than is the cal-

cium salt, and is less soluble than the barium trinitride. Analysis gave

	Calculated for SrN_6.	Found.
Strontium	51.05	51.21
Nitrogen	48.95	48.71

Barium Trinitride, $BaN_6.H_2O$.—Curtius has described[1] the anhydrous barium trinitride. Although we used the same method of preparation, the crystals contained water, as could be seen by gently heating the salt in a glass tube, and as is indicated by the analysis :

	Calculated for $BaN_6.H_2O$.	Found.
Barium	57.32	57.10
Nitrogen	35.14	35.01
Water	7.54	(Diff.) 7.89

The salt crystallizes in glistening needles which lose luster on standing. They explode with quite a loud report when heated, the particles shooting about like miniature rockets.

The trinitrides of this group are soluble in water, the solubility increasing with the rise in the atomic mass of the base. All of them explode when heated, the violence of the explosion diminishing as the strength of the base increases. They become basic when exposed to the air. The solutions of the trinitrides in water also slowly lose some hydronitric acid upon standing, and quickly become basic when heated upon the water-bath.

CRYSTALLOGRAPHIC NOTES BY A. C. GILL.

The following crystallographic notes on the salts of the acid HN_3 with the bases Li, Na, K, Rb, Cs, Ca, Sr, and Ba were made from a study of material furnished by Mr. C. H. Benedict of the Chemical Department of Cornell University.

Since the lithium and barium compounds crystallize with a molecule of water each, they are not strictly comparable with the others, though the fact in itself proves, of course, a certain difference in their character. The series of anhydrous alkali salts presents the not uncommon phenomenon that the sodium compound behaves differently in its crystallization from the corresponding compounds of K, Rb, and Cs. The latter three are

[1] *Loc. cit.*, p. 3032.

strictly isomorphous, as might have been predicted *a priori*. In the case of the alkaline earths, however, the unusual condition obtains that calcium acts more like strontium than does barium. The detailed observations made on the material in hand are as follows:

$LiN_3.H_2O$, *hexagonal* (?).—The fine colorless needles, one to three mm. in length, deliquesce on exposure to the air so that no measurements were obtained on the goniometer. The cross-section of these needles, as seen by setting them on end in wax under a microscope with low power objective, seems to be hexagonal or triangular, though the rapid deliquescence entirely rounds off the angles almost before an observation can be made. The crystals have parallel extinction with greatest optical elasticity in the direction of elongation. They are, thus, probably hexagonal and optically negative. The double refraction is very strong,—about 0.250 as determined by interference colors under crossed nicols.

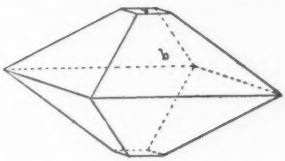
NaN_3, *hexagonal*.—Crystals of this substance exhibit a very varied habitus, but only the extremely thin basal plates, among the crystals studied, furnished any crystallographic data. These show irregular outlines, and have a diameter of one to two and one-half mm., with a thickness of 0.02 to 0.1 mm. Lines of cleavage making an angle of 60° (rarely 30°) are plainly visible in many places. In converged polarized light the optical interference figure is uniaxial and positive. The hexagonal form is thus established beyond question. The strength of the double refraction of this substance is remarkable, for a 0.1 mm. plate shows the colored rings of its interference figure much closer together than in a calcite plate two and one-half times as thick.

KN_3, *tetragonal*.—Brilliant colorless transparent crystals from two to five mm. in diameter gave excellent measurements on the goniometer. The shape of these is seen in the figure where p = the base, (001), and b = the pyramid (111). The axial ratio $a : c = 1 : 0.57976$. This is computed from twenty-one measurements of the angle 111 to $\bar{1}\bar{1}\bar{1}$ which varied from 78° 40′ to 78° 44′, averaging 78° 41′ 45″. The calculated polar angle 111 to $\bar{1}\bar{1}\bar{1}$ is 53° 16′ 34″; found, 53° 16′ 15″. The base is too rough to give good reflections, but is always present. The prism (110), on the other hand, is very rarely to be seen, but

in one case gave a sharp image in the telescope of the goniometer. The crystals are optically uniaxial, negative, and very strongly doubly-refracting.

RbN_3, *tetragonal.*—In general appearance these crystals differ from those of KN_3 only in having the basal plane more largely developed, so that their habitus is tabular rather than pyramidal. The angle from base (001) to pyramid (111) is about 40° 13′ (average of eleven measurements varying from 39° 51′ to 40° 35′) whence $a : c = 1 : 0.5979$. The double refraction is negative, like that of KN_3, but decidedly weaker.

CsN_3, *tetragonal.*—No good crystals for goniometric measurement were at hand, but under the microscope they showed themselves similar in shape to the preceding. They are uniaxial, negative, and weaker in double refraction than RbN_3. Under crossed nicols the interference colors of crystal fragments indicate a double refraction of 0.050. The basal plates are often



traversed by twin lamellae. One specimen having a sharp rectangular outline showed these lamellae at angles of 90° with each other, but turned 10° with reference to the outline of the crystal. Hence this substance, and probably the two foregoing, is very likely pyramidal hemihedral.

CaN_6, *orthorhombic* (?).—This substance was seen only in the shape of milk-white balls or spherules composed of radiating needles. On crushing, these showed under the microscope parallel extinction, with the greater elasticity in all cases in the direction of elongation of the needle. Since the double refraction appears to vary from 0.070 to 0.100, the substance is probably orthorhombic, rather than tetragonal or hexagonal.

SrN_6, *orthorhombic*, (?).—It resembles very closely the foregoing, and could be investigated only to the same limited extent. The double refraction is slightly stronger, and the spherulitic aggregates are less perfectly round than is the case with CaN_6.

$BaN_6 + H_2O$, *triclinic.*—The brilliant little crystals of the barium salt have a six-sided prismatic habitus, with terminating faces usually at only one end. The other end is frequently attached to another individual in twinning position, the long axes of the two making an angle of about 65°. The small size and irregular surface of the crystals prevented measurements of sufficient accuracy to determine the axial ratios. The angle which would be naturally chosen as that of the prism measures 66° 12′. Since the extinction angle is 22° when the obtuse interior angles of this prism are placed in a vertical plane one above the other, and 10½° when the crystal is turned 90° about its long axis, the crystal system must be triclinic. The double refraction is extremely high, above 0.200, and the mean index of refraction is about 1.7.

CORNELL UNIVERSITY,
JANUARY, 1898.

INTRODUCTORY NOTE ON THE REDUCTION OF METALLIC OXIDES, AT HIGH TEMPERATURES.

BY FANNY R. M. HITCHCOCK.

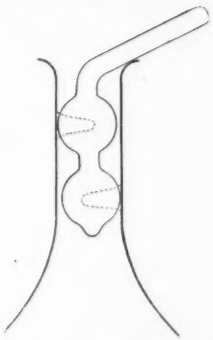
Received January 22, 1898.

A consideration of the results obtained by Dr. Friedheim and the author, when working on the atomic mass of tungsten in 1895, and 1896, led me to the conclusion that the loss in weight of the metallic oxides on reduction in hydrogen was not due solely to oxygen. Experiments made at high temperatures showed nitrogen was given off steadily though very slowly from tungstic oxide and from molybdic oxide, when reduced in a current of hydrogen. On decreasing the temperature the amount of nitrogen decreased ; on raising the temperature again, nitrogen was given off in greater quantities. While the spectrum of the gas gave only the appearance of nitrogen, and no trace of argon or helium could be found on sparking with oxygen, yet the densities were abnormal, and indicated the presence of gases both lighter and heavier than nitrogen. The nitrogen obtained on reduction in porcelain tubes at the temperature obtainable with a Glaser furnace gave densities varying from two to eight (H = 1). The gas obtained when a Lorenz furnace was used gave densities of from twenty-two to twenty-six.

In this latter gas argon may be present. The results obtained by an examination of the gas from different metallic oxides indicate that nitrogen is generally present in greater or less amounts; and the low results for atomic weights obtained by the reduction method might be thus easily accounted for. Ferric oxide, prepared from ferrous oxalate, which was made from pianoforte wire, showed a noticeable amount of nitrogen. The results obtained with other oxides will soon be ready to communicate; as the experiments are not completed and the examination of the gases is still under way, the author desires for the present to reserve this field of research.

NOTES.

Device to Prevent Loss from Spattering.—To prevent loss from spattering or bumping when boiling liquids in flasks, the writer



has devised the arrangement herein described, and found it to work very satisfactorily,—much more so than a watch-glass cover. The accompanying diagram is almost self-explanatory. Two bulbs are blown on the end of a piece of glass tubing which is then bent and finished as shown. The bulbs should fit quite loosely in the neck of the flask and the exterior handle should incline downward into the flask so as to return anything condensed thereon. It will be found that the escaping vapors will condense on the bulbs and form liquid joints at the points indicated by the dotted lines. As these joints are always on opposite sides of their respective bulbs, they form a complete obstruc-

tion to spattering liquids but allow gases to freely escape through the circuitous course around them.

The arrangement is especially useful in making copper assays where the sulphuric acid used in expelling the other acids frequently bumps badly. A single bulb, hanging well down in the neck of the flask, is often quite sufficient but two bulbs are better.

ALBERT H. LOW.

LABORATORY OF VON SCHULZ & LOW,
DENVER, COLO., JANUARY 20, 1898.

CORRESPONDENCE.

WASHINGTON, D. C., February 14, 1898.

Editor Journal of the American Chemical Society:

Dear Sir.—The Organization Committee of the Third International Congress of Applied Chemistry, which is to be held in Vienna during the coming summer, has fixed the date of the meeting from July 28, to August 2, 1898. Some time during the month of February, programs and announcements will be sent to all persons who have been enrolled as members of the Congress.

Respectfully,
H. W. WILEY,
Chairman of the American Committee.

WASHINGTON, D. C., February 23, 1898.

Editor Journal of the American Chemical Society:

Dear Sir.—The committee appointed by the president of the society, in harmony with the resolution of the board of directors adopted at the meeting of October 7, 1897, has considered the question of a want column in the Journal. We propose that such a column be opened in the Journal for the use of the members of the society who may desire to secure employment, and for the use of employers who may desire to secure the professional services of members of the society.

We therefore wish to announce to members seeking employment or new fields of labor, that they are invited to insert a notice to that effect in the advertising columns of the Journal, free

of charge, the notice not to exceed the space of three one-half inch insertions. We also desire to inform employers, companies, and corporations desiring the professional services of members of the society, that they may insert an advertisement to that effect, of the space of three one-half inch insertions in the columns of the Journal free of charge. The advertisements should be sent to the editor of the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Easton, Pa.

Respectfully,

H. W. WILEY,
CHARLES E. MUNROE,
F. W. CLARKE,

NEW BOOKS.

RESEARCHES ON THE MOLECULAR ASYMMETRY OF NATURAL ORGANIC PRODUCTS. By LOUIS PASTEUR, membre de la Société Chimique de Paris, (1860). Alembic Club Reprints, No. 14. Edinburgh: William F. Clay. 1897. Cloth. 46 pp. Price, 1s. 6d.

In presenting this important paper in English translation the Alembic Club has rendered a valuable service to chemists interested in the history of the rise and development of fruitful scientific theories. The study of the phenomena of rotary polarization of organic substances has led to the discovery of most important peculiarities in the constitution of the complex compounds of carbon, and in this paper by Pasteur we find described in a simple yet masterly style the several steps which led him up to his first great generalization on the subject of optical isomerism. In the early 40's he became engaged in a study of the relation of the crystalline forms of certain tartrates to their observed optical rotations. In 1848 he was able to announce the isolation of the right- and left-handed tartaric acids from ammonium sodium racemate; this pioneer discovery was followed by others published at frequent intervals, all of which attracted much attention. In 1860 the Chemical Society of Paris invited Pasteur to deliver two lectures covering the matter of his investigations in this field. The lectures were given in semi-popular form and published in the following year. The Alembic Reprint is simply the translation of the lectures as given in 1860. The translator very properly calls attention to

the fact that later investigations have not modified the theories advanced by Pasteur in any essential particular, and further that they must be considered as paving the way for the able and fruitful hypotheses of LeBel and van't Hoff on the relations of asymmetric carbon atoms, published many years later.

J. H. LONG.

A HANDBOOK FOR CHEMISTS OF BEET-SUGAR HOUSES AND SEED-CULTURE FARMS. BY GUILFORD L. SPENCER, D. Sc., of the U. S. Department of Agriculture. First Edition. New York: John Wiley & Sons. London: Chapman & Hall, Ltd. 1897. x + 475 pp. Price, $3.00.

This work is the outcome of the favorable reception accorded the author's Handbook for Sugar Manufacturers, and of the increased importance of beet-sugar manufacture in the United States.

In it are given short and easily understood directions for sampling and analyzing the raw material and products which the chemist of a beet-sugar house or seed-control farm has to deal with; many hints on sugar-house work and chemical control; and a very complete set of tables; all combining to make a handbook which cannot but be of service to the man of wide, as well as the man of limited experience. It is to be regretted that so many sugar-house managers think it economy to employ as chemists, men with a very limited knowledge of chemical theory and manipulation, but such is the case, and this handbook contains much that will prevent such men from going astray, as well as much to encourage further study.

I can endorse the author's statement that many so-called "undetermined losses" are due to errors in measuring, sampling, or methods of analysis. Throughout the book the author gives evidence of an appreciation of the difficulties in effecting chemical control—difficulties which the merely theoretical man is apt to overlook or underestimate.

EDMUND C. SHOREY.

A PRACTICAL TREATISE ON MINERAL OILS AND THEIR BY-PRODUCTS, INCLUDING A SHORT HISTORY OF THE SCOTCH SHALE OIL INDUSTRY, ETC. BY ILTYD I. REDWOOD. London: Spon; New York: Spon & Chamberlain. 8vo. 336 pp., with 67 illustrations. Price, $6.00.

The work opens with an interesting chapter upon the history of the subject, which is followed by a geographical and geolog-

ical description of the occurrence of shale. The theory of the process of manufacture is then discussed: it is shown that the oil does not exist in the shale as such but is formed by destructive distillation. This gives rise to oily bases and phenols which have to be removed. The refining of shale oil is therefore a much more difficult and delicate process than that of petroleum.

The main part of the book is taken up with the practical treatment: the operations of distilling, refining, treating, and pressing are minutely described and discussed, the size of the apparatus, the yield, and the costs being given. The by-products and recovered products, ammonia, soda, acid, and waste water, are next detailed.

The last chapter deals with the tests applied in the process, from time to time, and the laboratory method of testing wax, oil, and ammonia. The work closes with an appendix giving an abstract of all the patents which have been obtained in connection with this industry.

A. H. GILL.

A SHORT HANDBOOK OF OIL ANALYSIS. By AUGUSTUS H. GILL, S.B., PH.D. Philadelphia: J. B. Lippincott Co. 1898. Cloth. 139 pp. Price, $1.50.

This little volume is evidently written with the idea of furnishing students with brief outlines of the best methods of oil analysis known at the present time, and also short descriptions of the oils in common use, their properties and the sources from which they are derived.

As an introduction to the study of oils, and for practical use in the laboratory, it will be found an admirable text-book, while the copious reference notes will enable the student to readily follow the subject further, if he so desires.

Part I is devoted to the physical and chemical tests used to identify the various oils, determine their purity, and ascertain their fitness for a given purpose. Petroleum products are first discussed, one chapter being devoted to burning oils and the tests commonly applied to them, and another to lubricating oils. Then follows a chapter on animal and vegetable oils, and the tests used to identify them, determine their purity, and detect adulterants.

The author has rightly emphasized the desirability of having

samples of undoubted purity with which to compare the oil under process of identification, as even the so-called "constants" are so variable in the case of oils, that one may be easily misled, especially where only a small amount of an adulterant is present. On the general subject of lubrication the author is a little too brief to leave a clear impression in the mind of the student.

The rank which is given mineral oils as having greater adhesion and less cohesion than animal and vegetable oils is open to question, for while this may be true at ordinary temperatures, it will not be found the case when the parts requiring lubrication become warm from any cause, and the lubricant is most needed. At high temperatures nothing but the most viscous fat oil we can obtain will adhere to the heated surfaces, and it is for this reason that a percentage of an animal or vegetable oil is added to cylinder oils—in order to give the adhesiveness which is wanting in petroleum products at cylinder temperatures. This emphasizes the desirability of determining the viscosity of an oil at the temperature at which it is to be used.

Part II contains brief descriptions of the various oils in common use, giving their source, preparation, constants, adulterants, and uses, in a concise and comprehensive manner.

The appendix contains much valuable information in tabulated form. O. S. DOOLITTLE.

AN INTRODUCTORY COURSE IN QUANTITATIVE ANALYSIS. By PERCY W. EVANS, PH.D., Associate Professor of Chemistry, Purdue University. Boston: Ginn & Co. 1897. iv + 83 pp. Price, 55 cents.

The little book of Prof. Evans offers within a scope of eighty pages a very instructive course in quantitative analysis, including gravimetric and volumetric methods, together with a discussion of the various manipulations with which every student of this branch should become familiar as a preliminary. The exercises are well chosen and the explanations clear and comprehensive. As a handbook it might well find use in many college laboratories. F. C. PHILLIPS.

EXERCISES IN PRACTICAL PHYSIOLOGY. PART III. PHYSIOLOGY OF THE NERVOUS SYSTEM. ELECTRO-PHYSIOLOGY. By Augustus D. Waller, M.D., F.R.S. London, New York, and Bombay: Longmans, Green & Co. 91 pp. Price, 90 cents.

As the title indicates, this is a practical or laboratory hand-

book and is intended to accompany the third edition of the author's well-known "Introduction to Human Physiology." In ninety-one pages of matter the student, who is supposed to have had a year's training in general physiology, is given careful directions for performing a large number of important experiments relating to the physiology of the nervous system. The book makes no pretense to being anything more than a laboratory guide, and from this standpoint the selection of exercises it presents must be considered excellent and well chosen. Most of the experiments are adapted to the needs and understanding of that growing class of students in our medical schools which demands thorough training in physiology and chemistry as preliminary to a proper appreciation of clinical demonstrations, and to such students the book can be recommended.

J. H. LONG.

THE CHLORINATION PROCESS. By E. B. WILSON, E.M. New York: John Wiley & Sons. 1897. 12 mo. cloth. v + 125 pp. Price, $1.50.

This book was evidently written to meet the present demand for information regarding gold. It is mild to say that the work was poorly done. It is mainly an undigested mass of citations tied up with confused and misleading statements which injure the utility of even the best quotations.

The author's statements are often inexact and frequently contrary to fact. For instance, he uses "chlorine" as synonymous with "chloride" and "chlorination" with "chloridizing roasting." Also, page 23, he makes this astounding statement: "Copper sulphides can be readily freed from their sulphur by slow roasting at a moderate heat, with or without salt." And, page 87, he gives the reaction on bringing hydrogen sulphide gas into acid auric chloride solution as "$2AuCl_3 + H_2S + 2H_2O = 2Au + 6HCl + SO_3$."

One looks in vain for any critical discussion of the chlorination process and its particular field of application, or for any tests to determine whether a given ore would be suitable for this process. In fact, Dr. Godshall's article in the *Engineering and Mining Journal*, Jan. 6 and 13, 1894, is a far better guide in investigating the chlorination process than Wilson's book.

FREDERIC P. DEWEY.

ORGANIC CHEMISTRY FOR THE LABORATORY. BY W. A. NOYES, PH.D. Illustrated. xii + 257 pp. Easton, Pa.: The Chemical Publishing Co. Price, $1.50.

Several excellent works on the preparation of organic compounds have recently appeared and it can no longer be said that the absence of comprehensive guides of this kind is a cause for complaint. Some of these have been kindly received by the critics and now this latest addition seems to be wholly worthy of equal praise. After an examination of this volume one feels that it may without apology be placed beside the best of similar efforts, although it is not intended to occupy precisely the same field as other laboratory guides.

Professor Noyes has done this work in a systematic form and evidently with great care; he has made it comprehensive enough to include the best methods of preparing the principal classes of carbon compounds, not confining himself to single examples in any class. The result is a reference book which can be used by the student but which also presents much more than the average student will attempt to accomplish. It does not outline a course of study nor are the various preparations presented in the order which a student would be likely to follow. The work is essentially for reference, adapted to the needs of advanced workers and instructors, although no part is beyond the capacity of the ordinary student who may wish to select certain of its contents for his own use.

There are twelve chapters, dealing in the order named, with acids; acid derivatives; halogen compounds; nitro compounds; amines; hydrazo, azo, and diazo compounds; alcohols and phenols; aldehydes and ketones with their derivatives; sulphonic acids; hydrocarbons; miscellaneous compounds; and qualitative reactions and reagents.

The method of treatment of these subjects follows a uniform order. Each chapter opens with a general discussion of the principal methods relating to the group of compounds under consideration, and then follows the discussion, in detail, of typical compounds within the group. Under acids, nineteen distinct examples are fully discussed and other groups are treated with appropriate fulness. Each preparation is described systematically, beginning with a statement as to the general character of

the method, and the specific character of the preparation to be undertaken. Then comes a summary of the literature bearing upon the subject ; an exact statement of the kind and amounts of the materials required ; and finally a careful description of the operation to be performed. Graphic formulas are freely employed, and the author frequently takes occasion to point out some historical significance or some general application of the particular experiment under discussion. Cross references are numerous and the book is well indexed. In all, ninety-six separate preparations are fully described.

The mechanical work of the book has been well done, although the illustrations can hardly be called elegant. This criticism applies so frequently to scientific literature that it suggests the possibility of the employment of conventional designs for the representation of common forms of apparatus like flasks, burners, coolers, receivers, supports, washing and drying vessels, etc., which would admit of common use, would be inexpensive and would serve for illustration in a simple and understandable way. The book is not wholly free from typographical errors and an occasional "chemical idiom," but these detract in no way from the highly creditable character of the work, which will without doubt be well received and successfully realize the author's purpose.

W. E. STONE.

BOOKS RECEIVED.

Laboratory Experiments on the Class Reactions and Identification of Organic Substances. By Arthur A. Noyes, Associate Professor of Organic Chemistry in Massachusetts Institute of Technology, and Samuel P. Mulliken, Instructor in Organic Chemistry in Massachusetts Institute of Technology. Second, Thoroughly Revised Edition. Easton, Pa.: The Chemical Publishing Co. 28 pp. Price, 50 cents.

The Freezing-point, Boiling-point, and Conductivity Methods. By Harry C. Jones, Instructor in Physical Chemistry in Johns Hopkins University. Easton, Pa.: The Chemical Publishing Co. vii + 64 pp. Price, 75 cents.

Twenty-first Annual Report of the Connecticut Agricultural Experiment Station for 1897. Part II. Fertilizers. 93 pp. Part III. Mildew of lima beans ; Prevention of leaf-blight and leaf-spot of celery ; Cause and prevention of a fungus disease of the apple ; Investigations on a disease of carnations ; Literature of fungus disease. 64 pp. The Connecticut Agricultural Experiment Station, New Haven, Conn.

The Irish Potato. Bulletin No. 42. Texas Agricultural Experiment Station, College Station, Brazos Co., Texas. 16 pp.

Nitrogenous Feeding Stuffs. By C. L. Phelps. Bulletin No. 18. December, 1897. Storrs Agricultural Experiment Station, Storrs, Conn. 16 pp.

Analysis of Commercial Fertilizers and Paris Green. Bulletin of the Agricultural Experiment Station. Second Series, No. 49. Louisiana State University and Agricultural and Mechanical College, Baton Rouge, La. 42 pp.

Observations on Recent Cases of Mushroom Poisoning in the District. of Columbia, United States Department of Agriculture, Division of Botany, Washington, D. C. 24 pp.

The Proceedings of the Chemical and Metallurgical Society of South Africa. May, 1895-January, 1897. Vol. I. Edinburgh, R. W. Hunter: Johannesburg, S. A. R.: The Chemical and Metallurgical Society of South Africa, 12 Chamber of Mines Building. 348 pp.

Bibliography of the Metals of the Platinum Group—Platinum, Palladium, Iridium, Rhodium, Osmium, Ruthenium—from 1748–1896. By Jas. Lewis Howe. City of Washington: Smithsonian Institution. 1897. 318 pp.

Tobacco Soils of the United States: A Preliminary Report upon the Soils of the Principal Tobacco Districts. By Milton Whitney. Bulletin No. 11. U. S. Department of Agriculture, Division of Soils. Washington, D. C. 1898. 47 pp. and 13 plates.

Das optische Drehungsvermögen organischer Substanzen und dessen praktische Anwendungen. Bearbeitet von Dr. H. Landolt, unter mitwirkung von Dr. Schönrock, Dr. P. Lindner, Dr. F. Schütt, Dr. L. Berndt, Dr. T. Posner. Zweite gänzlich umgearbeitete auflage, mit eingedruckten abbildungen. Braunschweig: Friedrich Viewig und Sohn. 1898. xxiv+ 655 pp. Price M 18.

The Arrangement of Atoms in Space. By J. H. van't Hoff. Translated and edited by Arnold Eiloart. Second enlarged and revised edition. Longmans, Green & Co., London, New York, and Bombay. 1898. xi + 211 pp. Price $1.75

On Laboratory Arts. By Richard Threlfall, M. A. New York: The Macmillan Co. 1898. xii + 338 pp. Price $1.50.

ERRATUM.

In the last (February) issue of the Journal on page 101, line 10, for "damp mercury" read "damp air."